

PHOTOLYSIS OF ORGANOPOLYSILANES. THE REACTION OF SILYLENES WITH ALLYL ETHYL ETHER

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Summary

The reactions of photochemically generated dimethylsilylene, methylphenylsilylene, phenyl(trimethylsilyl)silylene, and mesityl(trimethylsilyl)silylene with allyl ethyl ether have been investigated. Irradiation of dodecamethylcyclohexasilane in the presence of allyl ethyl ether at 10°C afforded 2-ethoxy-1,1-dimethyl-1-silacyclopropane, while similar photolysis at 35°C gave allylethoxydimethylsilane. The reaction of methylphenylsilylene and phenyl(trimethylsilyl)silylene at 10°C gave the respective silacyclopropanes, but at high temperature afforded the corresponding rearranged allylic silane derivatives. The photolysis of tris(trimethylsilyl)mesitylsilane in the presence of allyl ethyl ether resulted in formation of thermally stable 2-ethoxymethyl-1-mesityl-1-trimethylsilyl-1-silacyclopropane which did not afford the rearranged allylethoxydisilane at 200°C.

Introduction

There has been considerable interest recently in the reactions of silylene species with functionally substituted olefins [1–5] such as alkenyl ethers and alkenyl halides. Recently, Tortorelli and Jones have reported that dimethylsilylene generated photochemically from dodecamethylcyclohexasilanes reacted with alkyl allyl ethers to give alkoxyallyldimethylsilanes [1]. More recently, Tzeng and Weber have also found the formation of allylic dimethylmethoxysilanes in the reaction of dimethylsilylene with allylic methyl ethers [5]. In these reactions, Jones et al. [1] have proposed the mechanism involving formation of zwitterionic intermediates which can react further, either by direct alkyl rearrangement or by cleavage into pairs of radicals which can then recombine. Weber et al. [5] also suggested the zwitterionic intermediate which undergoes {2,3}-sigmatropic rearrangement to give the carbon–oxygen insertion product.

We have demonstrated that phenyl(trimethylsilyl)silylene reacts with vinyl ethyl ether [4] and allyl ethyl ether [3] to give the respective silacyclopropanes. We thought that the reaction of photochemically generated dimethylsilylene with allylic ethers

might produce 2-alkoxymethyl-1,1-dimethyl-1-silacyclopropanes, which would isomerize thermally to give the observed allylic alkoxydimethylsilanes; i.e. it seemed unlikely to us that dimethylsilylene would react with the allylic ethers in a different way from that of phenyl(trimethylsilyl)silylene. In order to clarify this question, we investigated the reaction of dimethylsilylene, methylphenylsilylene, phenyl(trimethylsilyl)silylene, and mesityl(trimethylsilyl)silylene with allyl ethyl ether under various conditions.

Results and discussion

First we carried out the reaction of dimethylsilylene with allyl ethyl ether. When a solution of dodecamethylcyclohexasilane (I) [6] in the presence of allyl ethyl ether in pentane was irradiated with a low-pressure mercury lamp bearing a Vycor filter (254 nm), and with ice cooling *, only a trace amount of allylethoxydimethylsilane (II) [7] (less than 0.2% yield) was detected in the photolysis mixture by GLC analysis, in addition to 50% of the unchanged starting I. No other volatile products arising from the reaction of dimethylsilylene with allyl ethyl ether were detected by GLC analysis. However, treatment of the photolysis mixture with methanol after irradiation was stopped, gave two compounds, allylmethoxydimethylsilane (III) [5] and 1-ethoxy-2-(methoxydimethylsilyl)propane (IVa) in 1 and 3% yield, respectively (Scheme 1).

The formation of compounds III and IVa can best be understood in terms of the reaction of 2-ethoxymethyl-1,1-dimethyl-1-silacyclopropane (V) produced from dimethylsilylene with allyl ethyl ether, with methanol as shown in Scheme 1.

Interestingly, the photolysis of I in the presence of allyl ethyl ether in pentane at room temperature without cooling (35°C) afforded II in 4% yield, along with 7% of the starting cyclohexasilane I. Neither III nor IVa was observed after treatment of the resulting solution with methanol. This result indicates that silacyclopropane V isomerizes completely to give II at 35°C.

When we carried out the photolysis of I in allyl ethyl ether using a high-pressure mercury lamp, compound II was obtained in 4% yield. In all photolyses of I in the presence of allyl ethyl ether at higher temperature, compound II was always obtained, but only in low yields (3–5%); we never obtained yields of II as high as those reported (40–50% yield [1]).

The structures of II and III were confirmed by comparison of their retention times on GLC with authentic samples. The mass spectral data for II and III were also identical with those of the authentic samples. Compound IVa was identified by chemical transformation with MeLi to 1-ethoxy-2-(trimethylsilyl)propane (IVb) which was also readily obtained by an independent synthesis (eq. 1).

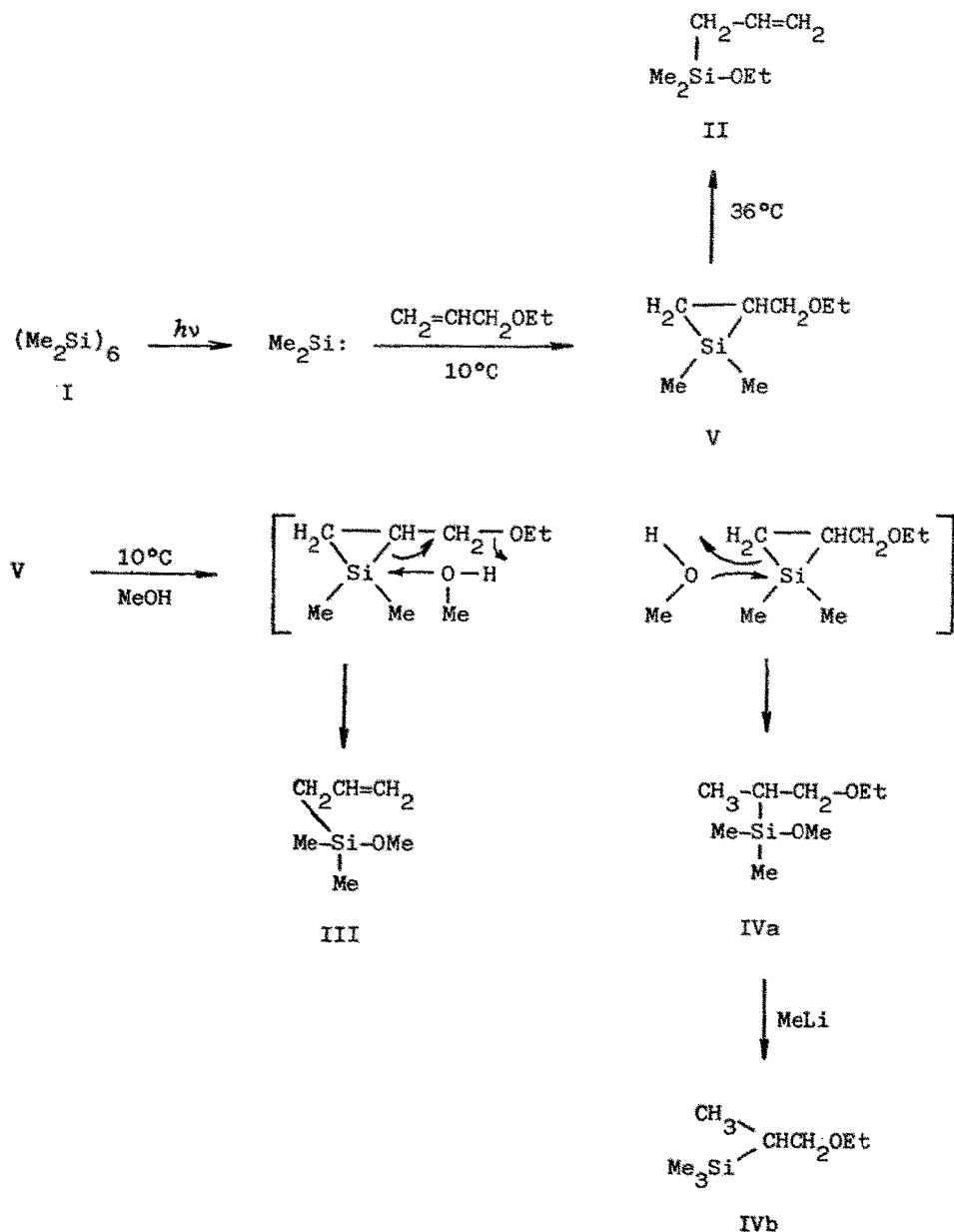


All spectral data for IVb thus formed were identical with those of the compound prepared from the reaction of 1-(trimethylsilyl)ethylmagnesium chloride with chloromethyl ethyl ether.

Methylphenylsilylene generated by irradiation of 2-phenylheptamethyltrisilane (VI) at 254 nm [8–10] also reacted with allyl ethyl ether at 10°C giving a silacyclo-

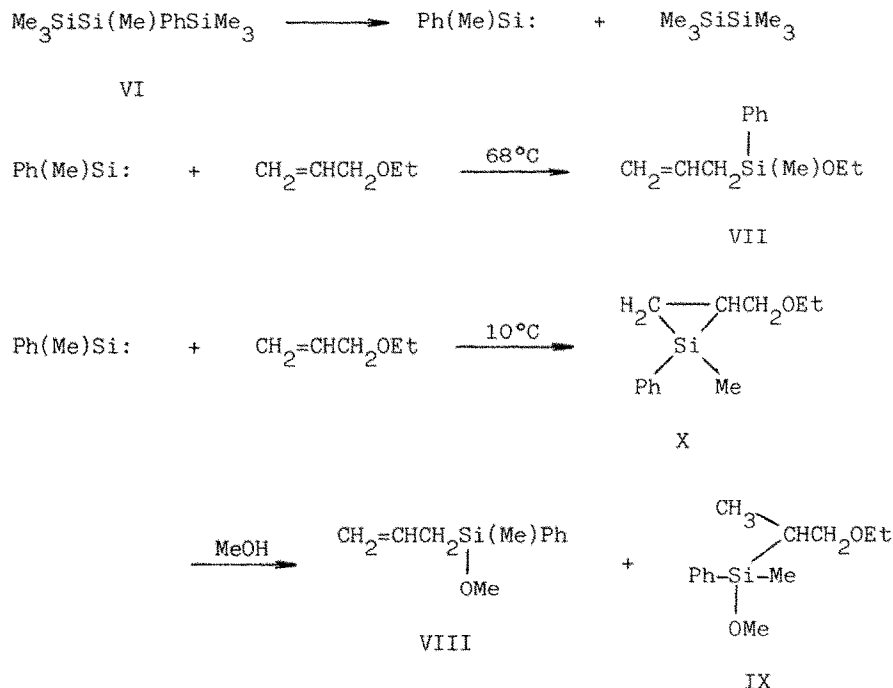
* Temperature of the photolysis mixture was determined to be 8–10°C during irradiation.

SCHEME 1



propane (X) as the sole product. Treatment of the photolysis mixture with methanol afforded both allylmethoxymethylphenylsilane (VIII) and 1-ethoxy-2-(methoxymethylphenylsilyl)propane (IX) produced from the reaction of silacyclopropane X with methanol, in 4 and 5% yield, respectively (Scheme 2). When a similar reaction was carried out at 68°C, allylethoxymethylphenylsilane (VII) arising from thermal isomerization of silacyclopropane X was obtained in 12% yield, as the sole volatile

SCHEME 2



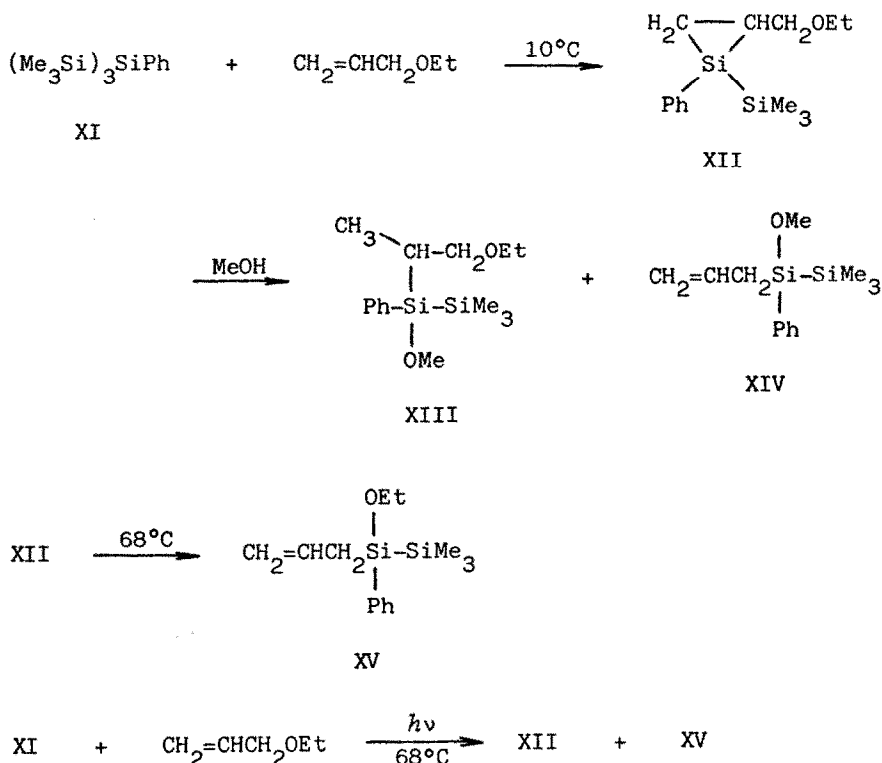
product. The fact that methanol treatment of an aliquot taken from this higher temperature photolysis mixture gave neither VIII nor IX indicates that thermal isomerization of silacyclop propane X to allylethoxysilane VII takes place readily at 68°C. The structures of VII, VIII and IX were verified by mass, IR, and ¹H NMR spectroscopic analyses and also by elemental analyses (see Experimental).

We have found that, in the reaction of silylene species with unsaturated carbon compounds, the silylenes bearing the bulkier substituents on the central silicon atom give better yields of addition products. For example, the reaction of phenyl(trimethylsilyl)silylene with olefins gives better yields of the adducts than those from the reaction of dimethylsilylene or methylphenylsilylene [11,12]. Therefore, we then carried out the reaction of phenyl(trimethylsilyl)silylene with allyl ethyl ether.

In our previous paper [3] it was shown that the photolysis of tris(trimethylsilyl)phenylsilane (XI) in the presence of allyl ethyl ether in hexane at 10°C produced 2-ethoxymethyl-1-phenyl-1-trimethylsilyl-1-silacyclop propane (XII) (19% yield) which reacted with methanol to give 1-ethoxy-2-(methoxyphenyltrimethyldisilanyl)propane (XIII) and 1-allyl-1-methoxy-1-phenyltrimethyldisilane (XIV). Similar photolysis of XI at higher temperature (68°C), however, gave 1-allyl-1-ethoxy-1-phenyltrimethyldisilane (XV) in 7% yield. In this photolysis, some of silacyclop propane XII survived in solution under the conditions used. Indeed, addition of methanol to the resulting photolysis mixture afforded XIII and XIV in 3 and 1% yield, respectively (Scheme 3).

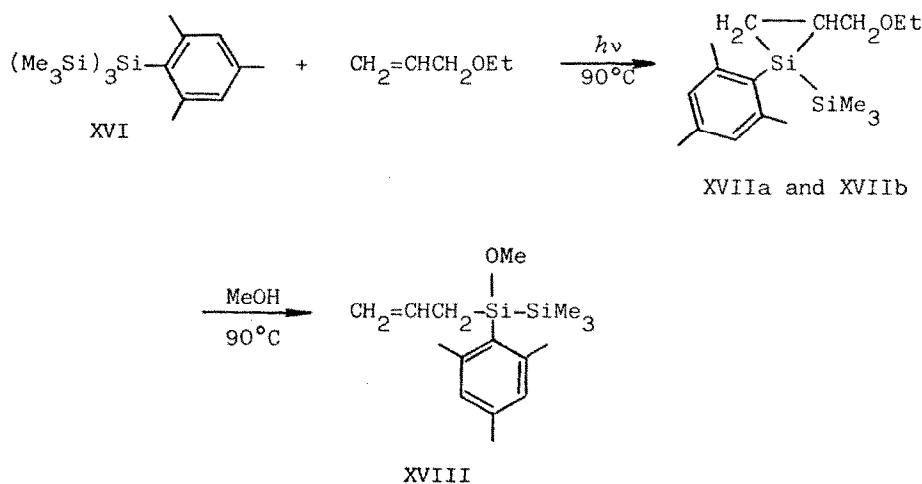
Interestingly, when a solution of XII prepared by the photolysis of XI in the presence of allyl ethyl ether in hexane at 10°C was heated at 68°C for 1 h, isomer XV was obtained in 16% yield on the basis of the starting silacyclop propane XII,

SCHEME 3



indicating that compound XV comes from thermal isomerization of silacyclopropane XII. No compound XIII was detected by GLC analysis after methanolysis of this solution, although a small amount of XIV produced by means of a methoxy/ethoxy exchange reaction of XV with methanol was observed. Unidentified polymeric substances were also obtained after distillation of the volatile product.

The reaction of mesityl(trimethylsilyl)silylene with allyl ethyl ether gave a thermally stable silacyclopropane in a good yield. Thus, irradiation of tris(trimethylsilyl)mesitylsilane (XVI) in the presence of allyl ethyl ether in a heptane solution at 10°C with a low-pressure mercury lamp afforded silacyclopropanes (XVIIa and XVIIb), which could be detected by GLC analysis as two peaks, in 20 and 23% yields, respectively, in addition to 24% of the starting compound XVI. Treatment of the resulting solution with methanol at 90°C , followed by GLC analysis showed the appearance of a new peak attributed to 1-allyl-1-mesityl-1-methoxytrimethyldisilane (XVIII) with the disappearance of two peaks corresponding to the silacyclopropanes XVIIa and XVIIb. Transformation of XVIIa and XVIIb into methoxysilane XVIII proceeded quantitatively. In this reaction, no other product analogous to IX or XIII was detected either by GLC analysis or spectroscopic analysis. Silacyclopropanes XVIIa and XVIIb could be distilled under reduced pressure, but all attempts to isolate them in a pure form using preparative GLC were unsuccessful, because of their kinetic instability. Nevertheless, silacyclopropanes XVIIa and XVIIb were



found to be thermally stable. Thus, when a mixture of crude XVIIa and XVIIb was heated at 200°C in a sealed tube for 5 h, XVIIa and XVIIb were recovered unchanged quantitatively.

In conclusion, the silacyclopropanes are initial products in the reaction of the silylenes with allyl ethyl ether. Allylethoxysilanes are produced by thermal rearrangement of the silacyclopropanes, but not zwitterionic intermediates, as recently proposed. The silacyclopropane bearing less bulky substituents on the ring silicon atom, such as 2-methoxymethyl-1,1-dimethyl-1-silacyclopropane V readily undergoes isomerization to give the allylethoxysilane at low temperature.

Experimental

General procedure

All reactions were carried out under an atmosphere of purified nitrogen. Photolysis was carried out using a low-pressure immersion mercury lamp bearing a Vycor filter (254 nm). All photolyses were followed by GLC analysis using a $1\text{ m} \times 0.5\text{ cm}$ glass column with Silicone DC-550 on Celite 545. Yields were determined by GLC using an internal standard on the basis of unrecovered starting polysilanes.

^1H NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solution 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. Infrared spectra of thin liquid films were determined using a Hitachi Model EPI-G3 grating infrared spectrophotometer. 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 $20\text{ ft} \times 3/8\text{ in.}$ column containing Silicone SE-30 (30%) on Celite 545.

The starting compounds, dodecamethylcyclohexasilane [6], 2-phenylheptamethyltrisilane [13], tris(trimethylsilyl)phenylsilane [11], and allylethoxydimethylsilane [7] were prepared by methods described in the literature.

Preparation of trichloromesitylsilane

In a 500-ml three-necked flask fitted with a stirrer, a dropping funnel, and a condenser was placed 37.5 g (0.22 mol) of silicon tetrachloride dissolved in 100 ml of ethyl ether. To this was added a mesityllithium-ether solution prepared from 4.3 g (0.62 g-atom) of finely cut lithium and 41.5 g (0.21 mol) of mesityl bromide over a period of 2 h with ice cooling. The mixture was stirred at room temperature for 5 h. Approximately 100 ml of ether was distilled off and the mixture was filtered off. The precipitates were washed with dry hexane. The filtrate and washings were combined and the solvents were evaporated. The residue was distilled under reduced pressure to give 20 g (38% yield) of white crystals: b.p. 86–88°C (0.5 torr); m.p. 50–52°C; mass spectrum m/e 252; ^1H NMR δ 2.31 ($p\text{-CH}_3$, s, 3H), 2.67 ($o\text{-CH}_3$, s, 6H), 6.92 ppm (ring protons, s, 2H) (Found: C, 42.45; H, 4.56; Cl, 41.65. $\text{C}_9\text{H}_{11}\text{Cl}_3\text{Si}$ calcd.: C, 42.62; H, 4.37; Cl, 41.93%).

Preparation of tris(trimethylsilyl)mesitylsilane (XVI)

In a 500-ml three-necked flask was placed 9.3 g (1.3 g-atom) of finely cut lithium and 97 g (0.89 mol) of trimethylchlorosilane in 200 ml of THF. To this solution was added 37.7 g (0.15 mol) of trichloromesitylsilane in 200 ml of THF over a period of 2 h at room temperature. After removing the excess lithium, the mixture was hydrolyzed with water. The organic layer was washed with water and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure to give 32 g of white crystals boiling over a range of 117–123°C (0.4 torr). Recrystallization of the crude crystals from ethanol gave 28.8 g (53% yield) of XVI: m.p. 84°C; IR 1247, 1609 cm^{-1} ; UV λ_{max} 246.9 nm ($\epsilon = 1.4 \times 10^4$); mass spectrum m/e 366; ^1H NMR δ 0.22 (Me_3Si , s, 27H), 2.21 ($p\text{-CH}_3$, s, 3H), 2.43 ($o\text{-CH}_3$, s, 6H), 6.71 ppm (ring protons, s, 2H) (Found: C, 58.71; H, 10.14. $\text{C}_{18}\text{H}_{38}\text{Si}_4$ calcd.: C, 58.93; H, 10.44%).

Photolysis of dodecamethylcyclohexasilane (I) in the presence of allyl ethyl ether at 10°C

In a 25-ml reaction vessel fitted internally with a low-pressure mercury lamp was placed a solution of 0.3610 g (1.04 mmol) of I, 21.0 mg (0.15 mmol) of decane, 54.2 mg (0.20) of nonadecane as internal standards, and 5 ml (45 mmol) of allyl ethyl ether in ca. 25 ml of pentane. The solution was irradiated for 20 min with a slow stream of nitrogen bubbling through the mixture with ice cooling. The GLC analysis of the photolysis mixture indicated that the presence of a trace amount of allylethoxydimethylsilane II (less than 2×10^{-3} mmol), in addition to 50% of the starting I. After the irradiation was stopped, 1 ml of dry methanol was added to the mixture, and the resulting solution was analyzed by GLC as being III (5×10^{-3} mmol) and IVa (1.3×10^{-2} mmol). Retention time on GLC column and gas chromatographic-mass spectrometric analysis of III were identical with those of an authentic sample; mass spectrum 130, 115, 89, 59. The mixture was concentrated and the residue was treated with 2 ml of 1.5 *M* methyllithium-ether solution. The mixture was allowed to stand for 2 h and then distilled under reduced pressure (15 torr) to give 1-ethoxy-2-(trimethylsilyl)propane (IVb). Pure IVb was isolated by preparative GLC. All spectral data for IVb were identical with an authentic sample.

Preparation of allylmethoxydimethylsilane (III)

In a 100-ml three-necked flask fitted with a condenser, a stirrer, and a dropping funnel was placed 7.2 g (60 mmol) of dimethoxydimethylsilane in 40 ml of ether. To this was added 60 ml of a 1.0 *M* allylmagnesium chloride-ether solution over a period of 20 min at room temperature. The mixture was stirred for 5 h at room temperature. The magnesium salts were filtered off and the filtrate was distilled using a short column to give 4.2 g (54% yield) of III [5]: b.p. 98–100°C; mass spectrum *m/e* 130; ¹H NMR δ 0.98 (Me₂Si, s, 6H), 1.5–1.7 (CH₂Si, m, 2H), 3.38 (MeO, s, 3H), 4.7–5.0 (CH₂=C, m, 2H), 5.5–6.0 ppm (C=CH–, m, 1H).

Preparation of 1-ethoxy-2-(trimethylsilyl)propane (IVb)

To 0.95 g (10 mmol) of chloromethyl ethyl ether in 10 ml of THF was added 7.0 ml of a 1.14 *M* 1-(trimethylsilyl)ethylmagnesium chloride-ether solution with ice cooling. The mixture was stirred for 1 h at 35°C and hydrolyzed with water. After evaporating the solvent, the residue was distilled to give crude IVb. Pure IVb (0.6 g, 48% yield) was separated by preparative GLC; IR 1251, 1121, 1103 cm^{–1}; ¹H NMR δ –0.03 (Me₃Si, s, 9H), 0.9–1.0 (CH₃CH, m, 4H), 1.14 (CH₃C, t, 3H, *J* 7 Hz), 3.2–3.5 ppm (CH₂O, m, 4H) (Found: C, 59.70; H, 12.80. C₈H₂₀OSi calcd.: C, 59.93; H, 12.57%).

Photolysis of I in the presence of allyl ethyl ether at 35°C

A mixture of 0.2942 g (0.843 mmol) of I, 21.2 mg (0.149 mmol) of decane, 20.8 mg (0.757 mmol) of nonadecane as internal standards, and 7 ml (63 mmol) of allyl ethyl ether in 25 ml of pentane was irradiated for 40 min at 35°C. The mixture was analyzed by GLC as being allylethoxydimethylsilane II (3% yield) and 7% of the unchanged starting I. Mass spectral data and retention time of II were identical with those of an authentic sample: mass spectrum *m/e* 129 (*M*⁺ – 15), 103, 75, 59.

Photolysis of 2-phenylheptamethyltrisilane (VI) in the presence of allyl ethyl ether at 10°C

A mixture of 0.9946 g (3.729 mmol) of VI, 0.0853 g (0.547 mmol) of undecane as an internal standard, and 5 ml (45 mmol) of allyl ethyl ether in 100 ml of hexane was irradiated for 1.4 h at 10°C. To the photolysis mixture was added 1 ml of dry methanol and the mixture was analyzed by GLC as being allylmethoxymethylphenylsilane VIII (4% yield), 1-ethoxy-2-(methoxymethylphenylsilyl)propane IX (5% yield) and 18% of the starting VI. Products VIII and IX were isolated by preparative GLC. For VIII: IR 1257, 1430, 1637 cm^{–1}; mass spectrum *m/e* 192; ¹H NMR δ 0.33 (MeSi, s, 3H), 1.7–1.9 (CH₂Si, m, 2H), 3.43 (CH₃O, s, 3H), 4.7–5.0 (CH₂=C, m, 2H), 5.6–6.0 (CH=C, m, 1H), 7.2–7.6 ppm (ring protons, m, 5H) (Found: C, 68.50; H, 8.62. C₁₁H₁₆OSi calcd.: C, 68.69; H, 8.39%). For IX: IR 1429, 1254 cm^{–1}; mass spectrum *m/e* 209 (*M*⁺ – C₂H₅); ¹H NMR δ 0.35 (MeSi, s, 3H), 0.9–1.3 (CH₃CH and CH₃C, m, 7H), 3.43 (CH₃O, s, 3H), 3.2–3.5 (CH₂OCH₂, m, 4H), 7.2–7.6 ppm (ring protons, m, 5H) (Found: C, 65.36; H, 9.12. C₁₃H₂₂O₂Si calcd.: C, 65.50; H, 9.30%).

Photolysis of VI in the presence of allyl ethyl ether at 68°C

A mixture of 0.4178 g (1.567 mmol) of VI, 58.5 mg (0.374 mmol) of undecane as an internal standard, and 5 ml of allyl ethyl ether in 20 ml of hexane was photolyzed

at 68°C for 50 min. The mixture was analyzed by GLC as being allylethoxymethylphenylsilane VII (12% yield) and 18% of the starting VI. Compound VII was isolated by preparative GLC: IR 1637, 1430, 1392, 1254, 1161, 1110, 1080 cm^{-1} ; mass spectrum m/e 206; ^1H NMR δ 0.35 (MeSi, s, 3H), 1.18 (CH_3C , t, 3H, J 7 Hz), 1.8–1.9 (CH_2Si , m, 2H), 3.67 (CH_2O , q, 2H, J 7 Hz), 4.7–5.0 ($\text{CH}_2=\text{C}$, m, 2H), 5.5–6.0 ($\text{CH}=\text{C}$, m, 1H), 7.2–7.6 ppm (ring protons, m, 5H) (Found: C, 69.66; H, 9.02. $\text{C}_{12}\text{H}_{18}\text{OSi}$ calcd.: C, 69.85; H, 8.79%).

Photolysis of tris(trimethylsilyl)phenylsilane (XI) in the presence of allyl ethyl ether at 68°C

A mixture of 0.3222 g (0.992 mmol) of XI, 72.91 mg (0.271 mmol) of nonadecane as an internal standard, and 5 ml (45 mmol) of allyl ethyl ether in 25 ml of hexane was photolyzed for 0.5 h at 68°C. The photolysis mixture was analyzed by GLC as being XV (7% yield) and 27% of the starting XI. To a solution (1 ml) of an aliquot taken from the photolysis mixture was added 50 μl of methanol. The mixture was analyzed by GLC as being XIII (3% yield) and XIV (1% yield). The retention times of XIII and XIV on various columns (Apiezon-L, SE-30, and Silicone-DC) were identical with those of authentic samples. Product XV was isolated by preparative GLC after concentration of the photolysis mixture. IR 1634, 1428, 1390, 1245, 1105, 1070 cm^{-1} ; mass spectrum m/e 264; ^1H NMR δ 0.13 (Me_3Si , s, 9H), 1.21 (CH_3C , t, 3H), 1.9–2.0 (CH_2Si , m, 2H), 3.70 (CH_2O , q, 2H), 4.7–5.0 ($\text{CH}_2=\text{C}$, m, 2H), 5.6–6.0 ($\text{CH}=\text{C}$, m, 1H), 7.2–7.6 ppm (ring protons, m, 5H) (Found: C, 63.37; H, 9.38. $\text{C}_{14}\text{H}_{29}\text{OSi}_2$ calcd.: C, 63.57; H, 9.15%).

Rearrangement of silacyclopropane (XII)

A solution containing 0.18 mmol of silacyclopropane XII prepared from the photolysis of a mixture of 0.3330 g (1.03 mmol) of XI, 0.3801 g (5.27 mmol) of allyl ethyl ether and 0.3503 g (0.12 mmol) of eicosan as an internal standard in 25 ml of hexane was refluxed for 1 h. The resulting mixture was analyzed by GLC as being XV (16% yield).

Photolysis of tris(trimethylsilyl)mesitylsilane (XVI) in the presence of allyl ethyl ether at 10°C

A mixture of 0.2516 g (0.686 mmol) of XVI, 30.1 mg (0.142 mmol) of pentadecane as an internal standard, and 5 ml (45 mmol) of allyl ethyl ether in 25 ml of hexane was photolyzed for 1.5 h at 10°C. After irradiation was stopped, 1 ml of methanol was added to the photolysis mixture. The mixture was heated at reflux temperature for 2 min and was analyzed by GLC as being XVIII (40% yield) and 38% of the starting XVI. Product XVIII was isolated by preparative GLC: IR 1635, 1611, 1246 cm^{-1} ; mass spectrum m/e 292; ^1H NMR δ 0.12 (Me_3Si , s, 9H), 2.0–2.1 (CH_2Si , m, 2H), 2.23 ($p\text{-CH}_3$, s, 3H), 2.37 ($o\text{-CH}_3$, s, 6H), 3.48 (CH_3O , s, 3H), 4.8–5.1 ($\text{CH}_2=\text{C}$, m, 2H), 5.6–6.1 ($\text{CH}=\text{C}$, m, 1H), 6.78 (ring protons, s, 2H) (Found: C, 65.83; H, 9.75. $\text{C}_{16}\text{H}_{28}\text{OSi}_2$ calcd.: C, 65.69; H, 9.65%).

Attempted rearrangement of silacyclopropane (XVIIIa and XVIIIb)

A mixture of 0.3114 g (0.849 mmol) of XVI, 37.8 mg (0.178 mmol) of pentadecane as an internal standard, and 2 ml of allyl ethyl ether in 25 ml of hexane was photolyzed for 2 h. The solvent hexane was distilled off under reduced pressure (1

torr) to give volatile products. The GLC analysis of the distillate showed the presence of 0.178 mmol of silacyclopropanes (XVIIa and XVIIb) in the ratio of 10/7, and 0.136 mmol of XVI, and trace amounts of other unidentified products. The distillate was sealed in a glass tube under reduced pressure and heated at 200°C for 5 h. The GLC analysis of the reaction mixture showed quantitative recovery of silacyclopropanes XVIIa and XVIIb.

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