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PHOTOLYSIS OF ORGANOPOLYSILANES. THE SYNTHESIS AND REACTIONS OF STABLE SILACYCLOPROPENES

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Summary

Two stable silacyclopropenes, 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropene and 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene, have been prepared by photolysis of 1,1-dimesityl-1-trimethylsilylethynyltrimethyldisilane and 1,1-dimesityl-1-phenylethynyldisilane, respectively. It has been found that these silacyclopropenes are not affected by atmospheric oxygen, moisture and alcohols at room temperature. 1-Mesityl-1-methyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene prepared by the photolyisis of 1-mesityl-1-phenylethynyltetramethyldisilane is rather stable toward atmospheric oxygen, but reacts readily with methanol in benzene to give a ring-opening methoxysilane. Photochemical and thermal behavior of these silacyclopropenes has been investigated.

Introduction

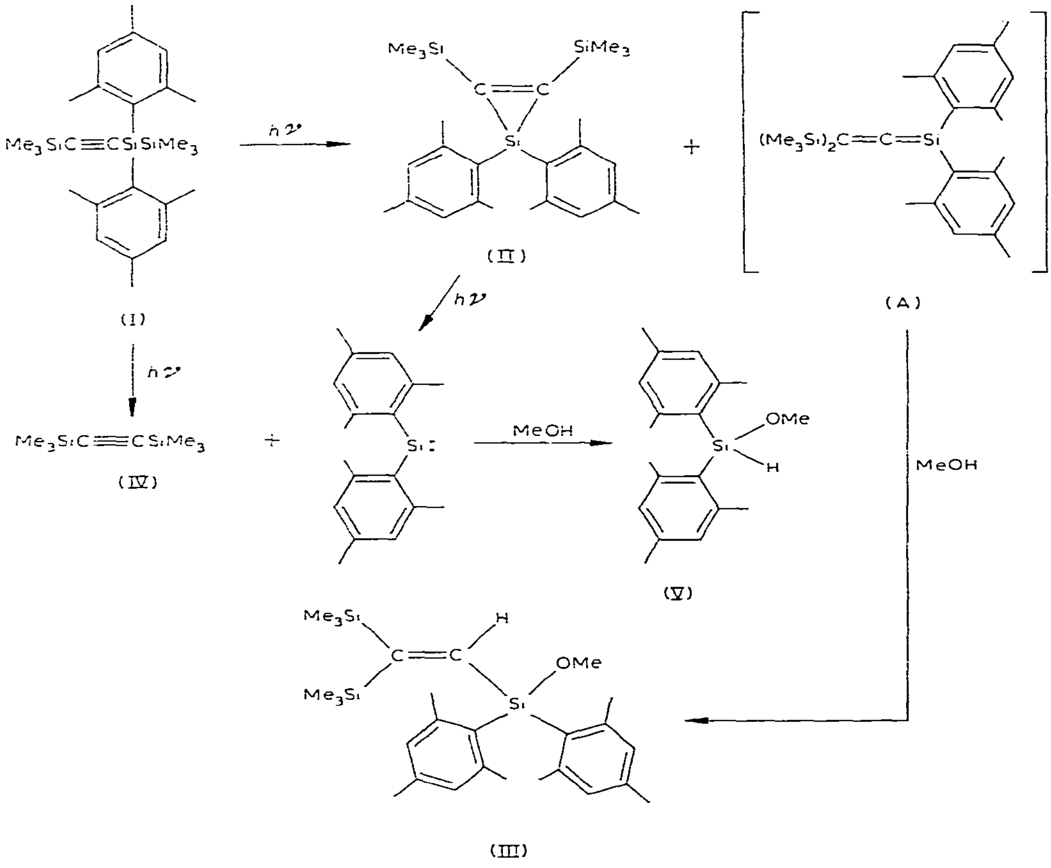
In previous papers of this series we reported two preparative routes to the silacyclopropenes [1—3]. One involves addition of photochemically generated trimethylsilylphenylsilylene to alkynes [1,3] and the other utilizes photolysis of phenylethynylpentamethyldisilane [2]. We have also presented evidence that introduction of bulky substituents onto both carbons and the silicon atom in the three-membered ring leads to the formation of silacyclopropenes which are rather stable toward methanol [3]. These observations encouraged us to prepare some stable silacyclopropenes which might be of great advantage to investigation of their chemistry.

Although many silacyclopropenes have been reported to date [4—7], all these compounds are extremely unstable toward atmospheric oxygen. On exposure to air, they immediately decompose to give non-volatile substances. In this paper, we report the synthesis of thermally and kinetically stable silacyclopropenes and some of their chemical behavior.

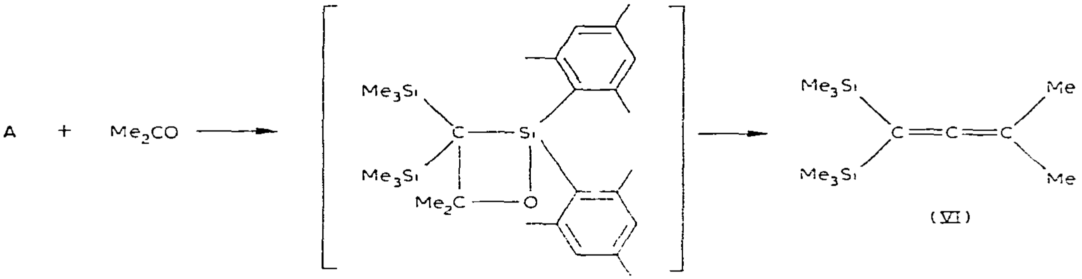
Results and discussion

We initially investigated the photochemical behavior of 1,1-dimesityl-1-trimethylsilylethynyltrimethyldisilane (I) in the presence of methanol. When a hexane solution of I was irradiated with a low-pressure mercury lamp bearing a Vycor filter for 2 h, 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropene (II) and 1,1-bis(trimethylsilyl)-2-dimesitylmethoxysilylethene (III) were isolated in 3 and 36% yield, respectively, in addition to 40% yield of bis(trimethylsilyl)-acetylene (IV) and 31% yield of dimesitylmethoxysilane (V) with 95% conversion of the starting disilane. The isolation of II is particularly surprising in view of the fact that all of the silacyclopropenes reported to date react readily with methanol to give the methoxysilanes. The formation of III can best be understood by the reaction of 1-silapropadiene intermediate (A) with methanol. Photochemical decomposition of either I or II yielding dimesitylsilylene results in the formation of IV. Insertion of dimesitylsilylene into the O—H bond of methanol affords compound V, as shown in Scheme 1.

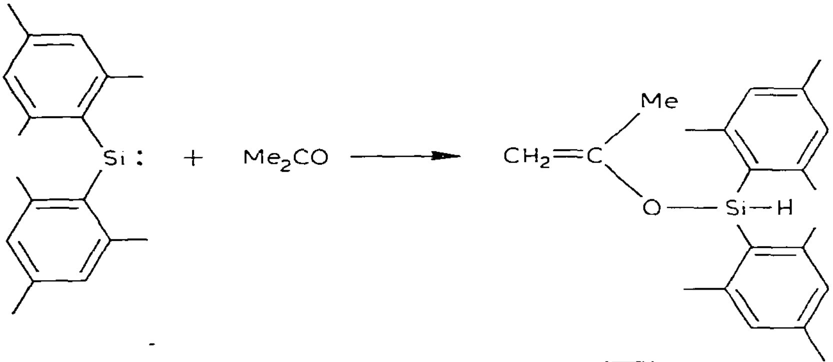
SCHEME 1



The intermediary formation of the 1-silapropadiene A could be confirmed by the photolysis of I in the presence of acetone. Thus, irradiation of I in the presence of acetone afforded 1,1-bis(trimethylsilyl)-3-methyl-1,2-butadiene (VI) in 23% yield. Again, silacyclopropene II was obtained in 14% yield, in addition to 35% yield of IV and 23% of the starting I. In this photolysis, silyl enol ether (VII), the product to be expected from the reaction of dimesitylsilylene with acetone also was obtained in 20% yield. The formation of silyl enol ethers from the reaction of silylene species with carbonyl compounds has been reported [8–10].



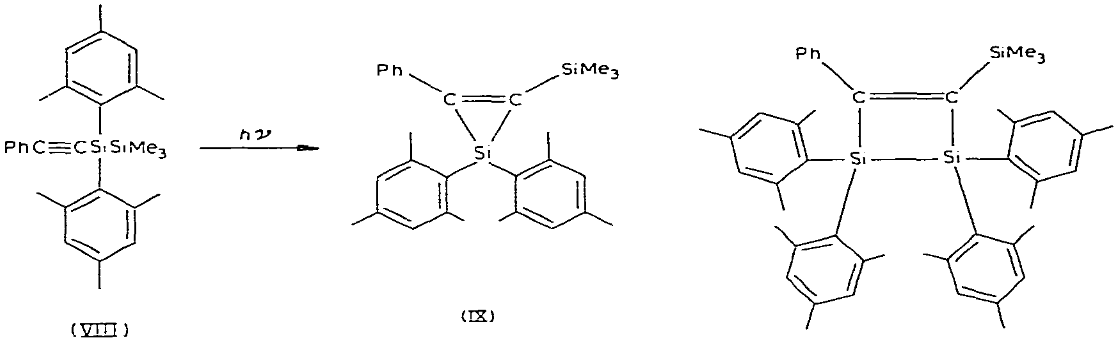
(VI)



(VII)

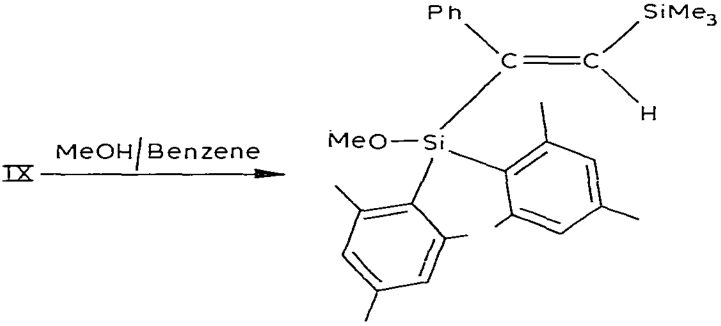
Irradiation of a hexane solution of I with a low-pressure mercury lamp for 1 h in the absence of a trapping agent produced an equilibrium mixture consisting of I and silacyclopropene II (50% combined yield) in a ratio of 3/2, in addition to 36% yield of IV, as the volatile products (vide infra). The silacyclopropene II could be isolated as colorless crystals by preparative TLC under atmospheric oxygen in 20% isolated yield. Surprisingly, compound II can be purified by recrystallization from ethanol. Furthermore, compound II is not affected by moisture and atmospheric oxygen.

We next examined the photolysis of 1,1-dimesityl-1-phenylethynyltrimethyldisilane (VIII) in the hope of obtaining another stable silacyclopropene. Irradiation of VIII with a low-pressure mercury lamp in hexane solution afforded 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (IX) in 65% yield, which could be isolated by preparative TLC in 49% yield, as a colorless liquid under atmospheric oxygen. In this photolysis, 1,1,2,2-tetramesityl-3-phenyl-4-trimethylsilyl-1,2-disilacyclobutene (X) (8% yield) and a small amount of phenyl(trimethylsilyl)acetylene were produced. No other product was detected by GLC or TLC analysis. Compound IX is also not affected by molecular oxygen, water and methanol in the presence or absence of the solvent at room temperature. However, when IX was refluxed in the presence of a large excess of



(VIII) (IX) (X)

methanol in benzene under atmospheric oxygen for 4 h, 1-dimesitylmethoxysilyl-1-phenyl-2-trimethylsilylethene (XI) was obtained in 58% yield, with 30% of the starting silacyclopropene IX being recovered. Structure proof of XI is as follows.



(XI)

The proton NMR spectrum of methoxysilane XI showed a resonance at δ 6.51 ppm due to the vinylic proton. To our knowledge, the chemical shift of the vinylic proton in the compounds which have the (*E*)-Ph(Si)C=C(Si)H structure shows a signal at δ 6.3—6.6 ppm, while the vinylic proton of the Ph(H)-C=C(Si)$_2$ appears at δ 7.5—7.8 ppm [2,11]. In methanolysis of silacyclopropanes or silacyclopropenes, methoxysilanes arising from the cleavage of the less substituted carbon—silicon bond in the three-membered ring are obtained as main products [12]. In the present case, a steric interaction between the bulky mesityl group and the trimethylsilyl group, which is significant enough to make the ring Si—C bond weaker is responsible for the preferential formation of XI.

The structures of silacyclopropenes II and IX were confirmed by IR, mass and proton NMR spectrometric analysis. The mass spectrum of II showed the parent peak at 436.2440, corresponding to the calculated molecular weight for II (436.2438). The proton NMR spectrum of II in CCl_4 showed four singlets in the ratio of 9/3/6/2, as expected, at δ 0.23, 2.21, 2.36, and 6.67 ppm, due to

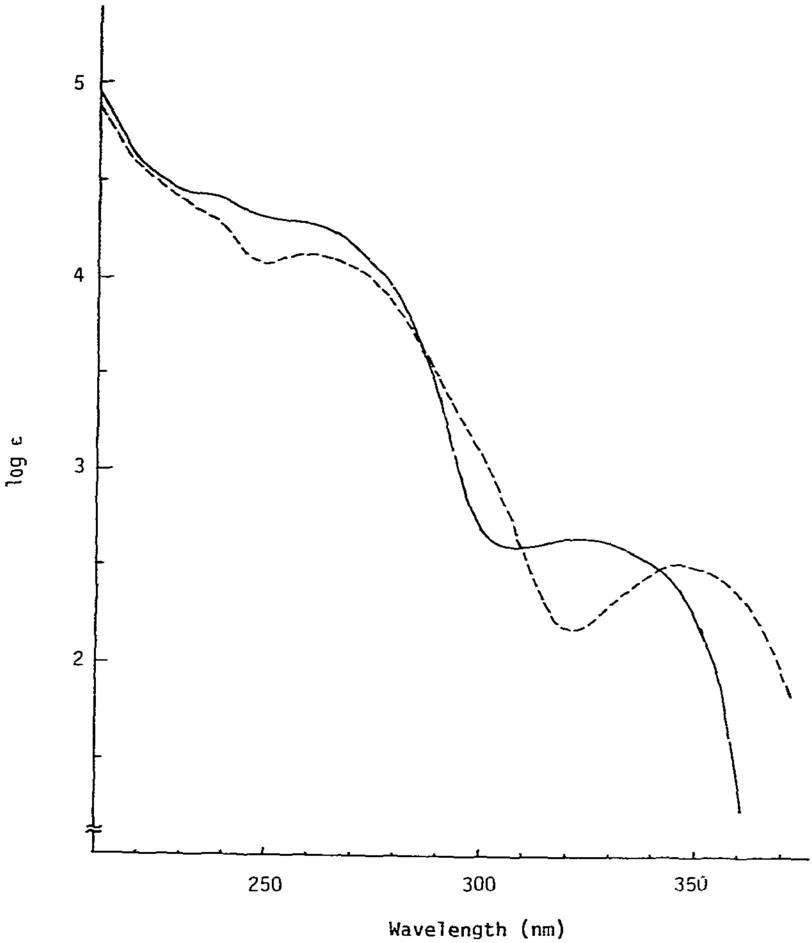


Fig. 1. UV spectra of silacyclopropenes II and IX; II - - - - - -, IX ———.

the Me—Si, *p*-Me—C, *o*-Me—C and ring protons, respectively. The exact mass of IX (440.2363) was identical with its calculated molecular weight (440.2356). The NMR spectrum of IX showed five peaks in the ratio of 9/6/12/4/5 at δ 0.30 (Me—Si), 2.21 (*p*-Me—C), 2.39 (*o*-Me—C), 6.69 (mesityl ring protons) and

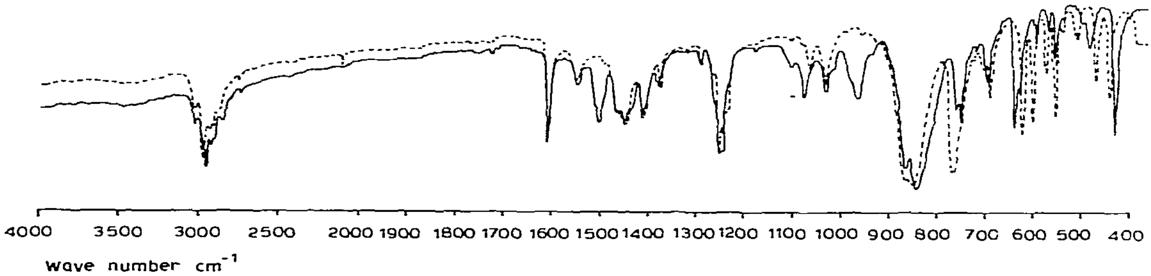


Fig. 2. IR spectra of silacyclopropene II and its precursor I; II ———, I - - - - - -.

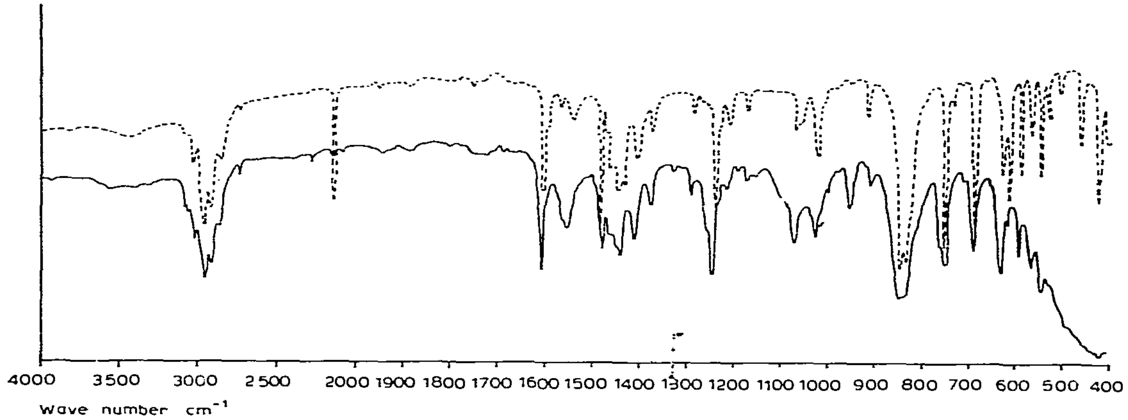
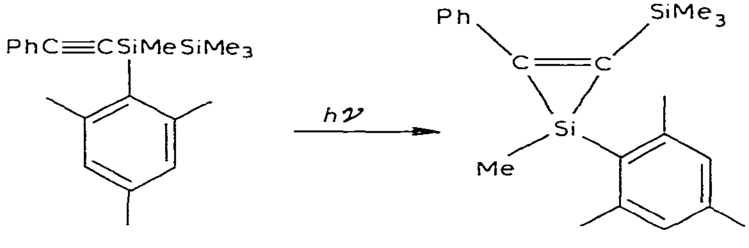


Fig. 3. IR spectra of silacyclopropene IX and its precursors VIII; IX ———, VIII - - - - - -.

7.1—7.6 ppm (phenyl ring protons), respectively.

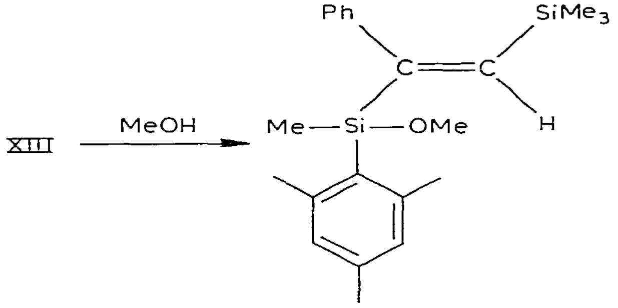
The UV spectrum of compound II shows absorptions at λ_{max} (ϵ) 238 (19500), 260 (13180) and 345 nm (325), and compound IX exhibits absorptions at λ_{max} (ϵ) 238 (25120), 258 (19500) and 322 nm (440), as shown in Fig. 1. The absorption with low intensity analogous to λ_{max} 345 nm for II and 322 nm for IX has been found in the UV spectrum of 1,1-dimethyl-2,3-bis-(trimethylsilyl)-1-silacyclopropene [5]. The IR spectra of compounds II and IX are shown in Figs. 2 and 3, with those of their precursors. As can be seen in these Figures, compound II shows characteristic bands of medium intensity at 1055 and 1510 cm^{-1}, and IX exhibits such bands at 1555 and 1560 cm^{-1}. We assigned these bands tentatively to the C=C stretching frequencies in the silacyclopropene rings.

1-Mesityl-1-methyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (XIII) was also prepared in 63% yield by the photolysis of 1-mesityl-1-phenylethynyltetramethyldisilane (XII) in hexane. Compound XIII is kinetically rather stable. Treatment of XIII with acetone for 24 h at room temperature produced no



(XII) (XIII)

two-atom insertion product, the starting XIII being recovered quantitatively, although when a 0.1 *M* hexane solution of XIII was exposed to air at room temperature, a slow decomposition giving non-volatile substances was observed. The half-life of XIII was determined to be 24 h by GLC analysis. Methanolysis of XIII, however, proceeded rapidly to give a ring-opened methoxysilane. Thus, treatment of XIII with a 50-fold excess of methanol in hexane solution afforded methoxysilane XIV quantitatively within a few minutes.



(XIV)

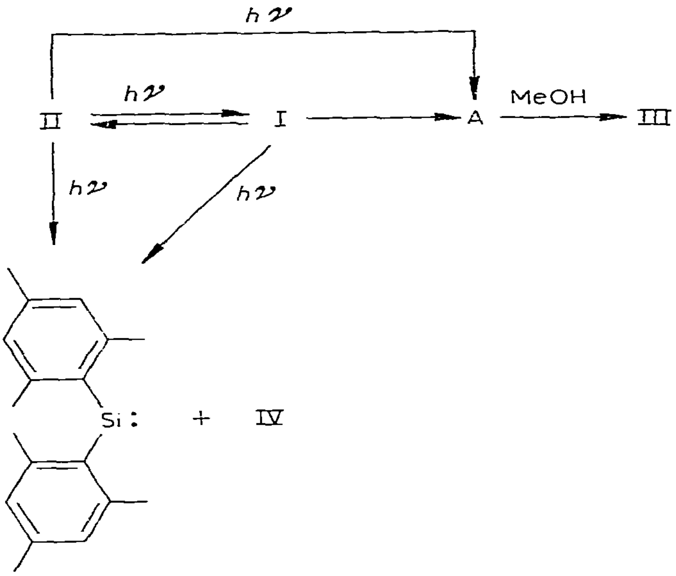
The proton NMR spectrum of XIV showed a sharp singlet resonance at δ 6.38 ppm, indicating that XIV must have the structure analogous to that of XI.

Photochemical behavior of II and IX

The photolysis of II has been found to proceed simultaneously by three different routes, one of which involves photo-isomerization to the starting disilane I, and the other two comprise the formation of silapropadiene A and the extrusion of dimesitylsilylene. Irradiation of II in benzene with a low-pressure mercury lamp for 10 h afforded an equilibrium mixture of I and II in the ratio of 3/2 (50% combined yield), in addition to 36% yield of IV. The total amounts of I and II decreased with increasing irradiation time, but the ratio of 3/2 did not change. Irradiation of II in the presence of methanol under similar photolysis conditions gave methoxysilanes III and V in yields of 14 and 32%, respectively, together with compound IV (60% yield), when conversion of II was 100%. These results clearly indicate that silacyclopropene II is transformed photochemically into I giving an equilibrium mixture and that I thus formed is photolyzed to yield the silicon—carbon double-bonded intermediate A as shown in Scheme 2. Irradiation of a benzene solution of II in the presence of methanol with a high-pressure mercury lamp bearing a Pyrex filter for 5 h afforded I, III and V in 60, 16 and 20% yield, respectively, indicating that compound II could be also transformed directly into intermediate A. In this photolysis, disilane I was found to be stable. Such transformation of the silacyclopropene into the silapropadiene in a different system has been mentioned briefly in a recent review article [13].

In sharp contrast to II, the photolysis of IX does not involve the reverse reaction to the phenylethynyldisilane VIII, but only the silylene extrusion takes place. Thus irradiation of IX in hexane afforded yellow crystals of 1,2-disilacyclobutene X (3.4% yield), arising from the reaction of IX with dimesitylsilylene, in addition to 5.1% yield of phenyl(trimethylsilyl)acetylene. Insertion of dimethylsilylene into a C—Si bond in the silacyclopropene ring under thermolysis conditions has been reported [14,15]. Compound X thus obtained is also stable toward atmospheric oxygen and moisture. It can be stored under atmospheric oxygen without decomposition.

SCHEME 2



Thermal behavior of II and IX

The thermolysis of II and IX in a degassed sealed tube was examined at 250°C. Interestingly, on heating II for 15 h, 60% of it was thermolyzed to give trimethylsilylethynyldisilane derivative I. After a 55 h reaction time, transformation into I was quantitative. Silacyclopropene IX seemed thermally more stable, as indicated by the fact that heating of IX for 40 h under identical conditions resulted in only 36% decomposition, with the remainder being recovered unchanged. In this case, phenyl(trimethylsilyl)acetylene (16% yield) was obtained as the sole volatile product, indicating the formation of silylene species.

Similar thermolysis of XIII for 30 h led to 50% decomposition. However, no volatile product was detected by GLC analysis.

Experimental

General procedure

All photolyses were carried out under an atmosphere of purified nitrogen. Proton NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane (δ 1.44 ppm) as an internal standard. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system. Ionizing voltage was 24 eV for all compounds. Ultraviolet spectra were measured in cyclohexane on a Hitachi EPS-3T spectrophotometer. Infrared spectra were determined using a Hitachi Model EPI-G3 Grating infrared spectrometer.

An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the products, III, V, VI, VII and XIV. They were easily separated as colorless liquids by using a 3/8 in × 20 ft column containing SE-30 Silicone oil (30%) on Celite 545. Preparative thin layer chromatography was carried out for isolation of II, IX, X and XI using silica gel 60 PF_{254}.

Yields were calculated on the basis of the starting substances used.

Materials

Trimethylsilylacetylene [16], 1,1-dichlorotetramethyldisilane [17] and 1,1,1-trichlorotrimethyldisilane [18] were prepared as reported in the literature.

Preparation of 1,1-dimesityl-1-trimethylsilylethynyltrimethyldisilane (I)

In a 300-ml three-necked flask was placed a solution of 15 g (0.07 mol) of 1,1,1-trichlorotrimethyldisilane in 100 ml of dry ether. To this was added a solution of mesityllithium prepared from 31.6 g (0.16 mol) of mesitylbromide and 3.3 g (0.48 g-atom) of lithium in 100 ml of ether at room temperature. The solvent ether (ca. 120 ml) was distilled off and the mixture was refluxed for 24 h. To this mixture was then added a solution of trimethylsilylethynyllithium prepared from 10 g (0.10 mol) of trimethylsilylacetylene and 55 ml of butyllithium/hexane solution (1.6 *M*) at —70° C. The reaction mixture was refluxed for 30 h and the mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over potassium carbonate. Distillation gave 12.6 g (40% yield) of I, b.p. 182° C/2 Torr, m.p. 105.5—107° C (after recrystallization from ethanol); M^+ 436 (mol. wt. 436.86); NMR (δ, ppm) 0.17 (Me_3Si, s, 9H), 0.24 (Me_3Si, s, 9H), 2.22 (*p*-Me—C, s, 6H), 2.34 (*o*-Me—C, s, 12H), 6.66 (ring protons, broad s, 4H) (Found: C, 71.17; H, 9.28. $C_{26}H_{40}Si_3$ calcd.: C, 71.47; H, 9.23%).

Preparation of 1,1-dimesityl-1-phenylethynyltrimethyldisilane (VIII)

In a 300-ml three-necked flask was placed 11 g (0.053 mol) of 1,1,1-trichlorotrimethyldisilane in 50 ml of ether. To this was added a solution of mesityllithium prepared from 28.5 g (0.14 mol) of mesityl bromide and 3.2 g (0.46 g-atom) of lithium in 100 ml of ether. After the solvent ether was distilled off, the mixture was refluxed for 20 h. To this mixture was added phenylethynyllithium prepared from 8 g (0.078 mol) of phenylacetylene and 42 ml of butyllithium/hexane solution (1.6 *M*). After 30 ml of tetrahydrofuran was added to the mixture, it was refluxed for 3 h. The reaction mixture was then hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over potassium carbonate. Distillation gave 8.5 g (36% yield) of crude VIII, b.p. 202—220° C/2 Torr, which crystallized on standing. Recrystallization from ethanol afforded 5.2 g (22% yield) of VIII, m.p. 111—112° C; M^+ 440 (mol. wt. 440.78); NMR (δ, ppm) 0.26 (Me_3Si, s, 9H), 2.21 (*p*-Me—C, s, 6H), 2.38 (*o*-Me—C, s, 12H), 6.68 (mesityl ring protons, s, 4H), 7.1—7.5 (phenyl ring protons, m, 5H) (Found: C, 79.09; H, 8.24. $C_{29}H_{36}Si_2$ calcd.: C, 79.02; H, 8.23%).

Preparation of 1-mesityl-1-phenylethynyltetramethyldisilane (XII)

This compound was prepared in 74% yield from 4 g (0.021 mol) of 1,1-

dichlorotetramethyldisilane, 0.035 mol of mesityllithium and 0.033 mol of phenylethynyllithium in a similar way to that described above, b.p. 164—168°C/2 Torr; M^+ 336 (mol. wt. 336.63); IR (cm^{-1}) 2155; NMR (δ, ppm) 0.20 (Me_3Si, s, 9H), 0.65 (MeSi, s, 3H), 2.23 (*p*-Me—C, s, 3H), 2.51 (*o*-Me—C, s, 6H), 6.73 (mesityl ring protons, broad s, 2H), 7.1—7.5 (phenyl ring protons, m, 5H) (Found: C, 74.74; H, 8.45. $C_{21}H_{28}Si_2$ calcd.: C, 74.93; H, 8.38%).

Photolysis of I in the presence of methanol

In a 25-ml reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed a mixture of 0.3111 g (0.71 mmol) of I, 0.0615 g (0.27 mmol) of cetane, 0.0369 g (0.29 mmol) of nonane as internal standards and 1 ml of dry methanol in 23 ml of dry hexane. The solution was irradiated at room temperature with a slow stream of nitrogen bubbling through the mixture. After 2 h irradiation, 95% of the starting I was photolyzed. The yields of the products, II (3% yield), III (36% yield), IV (40% yield) and V (31% yield) were determined by analytical GLC. Most of the solvent was evaporated, and the residue was distilled under reduced pressure to give volatile products boiling up to 220°C/2 Torr. Pure compounds III and V were isolated by preparative GLC. For III, exact mass (M^+ — 15) 453.2467 (calcd.: 453.2465); IR (cm^{-1}) 1105; NMR (δ, ppm) 0.09 (Me_3Si, s, 18H), 2.21 (*o*- and *p*-Me—C, broad s, 18H), 3.42 (Me—O, s, 3H), 6.70 (ring protons, broad s, 4H), 7.61 (vinylic proton, s, 1H). For V, exact mass 298.1774 (calcd.: 298.1753); IR (cm^{-1}) 1075, 2130; NMR (δ, ppm) 2.22 (*p*-Me—C, s, 6H), 2.32 (*o*-Me—C, s, 12H), 3.47 (Me—O, s, 3H), 5.72 (H—Si, s, 1H), 6.68 (ring protons, broad s, 4H).

Photolysis of I in the presence of acetone

A mixture of 0.3247 g (0.74 mmol) of I, 0.0629 g (0.28 mmol) of cetane, 0.0374 g (0.29 mmol) of nonane and 0.2 ml of acetone in 23 ml of hexane was photolyzed for 1 h. The mixture was analyzed by GLC as being II (14% yield), IV (35% yield), VI (23% yield), VII (20% yield) and 23% of the starting disilane I. Products VI and VII were isolated by preparative GLC. For VI, exact mass 212.1408 (calcd. 212.1415); IR (cm^{-1}) 1935; NMR (δ, ppm) 0.08 (Me_3Si, s, 18H), 1.63 (Me—C, s, 6H). For VII, exact mass 324.1902 (calcd. 324.1908); IR (cm^{-1}) 1040, 1075, 2150; NMR (δ, ppm) 1.81 (Me—CO, s, 3H), 2.25 (*p*-Me—C, s, 6H), 2.35 (*o*-Me—C, s, 12H), 4.00 (CH_2=C, broad s, 2H), 5.91 (H—Si, s, 1H), 6.70 (ring protons, broad s, 4H).

Preparation of silacyclopropene II

A mixture of 0.2872 g (0.66 mmol) of I and 0.0600 g (0.27 mmol) of cetane in 25 ml of hexane was irradiated for 1 h. At this stage 70% of the starting disilane I was photolyzed. The solvent hexane was distilled off and silacyclopropene II which remained in the residue was separated by preparative TLC to give 0.057 g (20% yield) of II, m.p. 114°C (after recrystallization from ethanol); exact mass 436.2440 (calcd.: 436.2438) (Found: C, 71.28; H, 9.04. $C_{26}H_{40}Si_3$ calcd.: C, 71.47; H, 9.23%).

Photolysis of II in the presence of methanol with a low-pressure mercury lamp

In a carefully dried 5-ml quartz tube was placed a solution of 10 mg of II, 2 mg of octadecane, 0.5 ml of methanol in 1 ml of dry benzene. The solution was purged with dry nitrogen and the tube was sealed with a serum cap. It was then irradiated externally with a low-pressure mercury lamp at room temperature for 15 h. The reaction mixture was analyzed by GLC as being III (14% yield), IV (60% yield), and V (32% yield).

Photolysis of II in the presence of methanol with a high-pressure mercury lamp

In a similar quartz tube to that used above was placed a mixture of 7.9 mg of II, 1.6 mg of eicosane and 0.3 ml of methanol dissolved in 1 ml of dry benzene. The mixture was then irradiated externally with a mercury lamp with Pyrex filter for 5 h. The resulting mixture was analyzed by GLC as being I (60% yield), methoxysilane III (16% yield) and methoxysilane V (20% yield).

Preparation of silacyclopropene IX

A mixture of 0.2316 g (0.53 mmol) of VIII and 0.0177 g (0.063 mmol) of eicosane and 0.0275 g (0.15 mmol) of tridecane in 23 ml of hexane was irradiated for 40 min at room temperature. At this stage, the starting disilane VIII was completely photolyzed. GLC analysis of the photolysis mixture showed the formation of phenyl(trimethylsilyl)acetylene (10% yield) and silacyclopropene IX (65% yield). The solvent hexane was distilled off and the products were separated by preparative TLC to give 0.1142 g (49% yield) of IX and 0.0143 g (8% yield) of 1,2-disilacyclobutene X as yellow crystals. For IX, exact mass 440.2363 (calcd.: 440.2356) (Found: C, 78.81; H, 8.37. $C_{29}H_{36}Si_2$ calcd.: C, 79.02; H, 8.23%). For X, m.p. 203—205°C; M^+ 706 (mol. wt. 707.24); NMR (δ, ppm) —0.13 (Me_3Si, s, 9H), 2.00 (*o*-Me—C, s, 12H), 2.11 (*p*-Me—C, s, 6H), 2.16 (*p*-Me—C, s, 6H), 2.36 (*o*-Me—C, s, 12H), 6.38 (mesityl ring protons, s, 4H), 6.56 (mesityl ring protons, s, 4H), 6.6—7.2 (phenyl ring protons, m, 5H) (Found: C, 80.01; H, 8.32. $C_{47}H_{58}Si_3$ calcd.: C, 79.82; H, 8.27%).

Photolysis of silacyclopropene IX

A solution of 0.3045 g (0.69 mmol) of IX and 0.0532 g (0.19 mmol) of eicosane in 25 ml of hexane was irradiated for 1.5 h. At this stage, 33% of IX was photolyzed. The volatiles were distilled away and the products in the residue were separated by preparative TLC giving 0.0084 g (3.4% yield) of X, in addition to 0.0884 g (29% yield) of IX.

Reaction of silacyclopropene IX with methanol

In a 10-ml flask was placed a mixture of 0.0313 g (0.071 mmol) of IX, 0.0069 g (0.025 mmol) of eicosane and 1 ml of methanol in 7 ml of benzene. The mixture was refluxed for 4 h. The GLC analysis of the reaction mixture indicated the formation of methoxysilane XI in 58% yield, in addition to 30% of the starting silacyclopropene IX. Compound XI was isolated by preparative TLC. Exact mass 472.2609 (calcd.: 472.2618); IR (cm^{-1}) 1095; NMR (δ, ppm) —0.22 (Me_3Si, s, 9H), 2.21. 2.23 (*o*- and *p*-Me—C, s, 18H), 3.14 (Me—O, s, 3H), 6.51 (vinylic proton, s, 1H), 6.65 (mesityl ring protons, s, 4H), 6.8—7.1 (phenyl ring protons, m, 5H).

Photolysis of 1-mesityl-1-phenylethynyltetramethyldisilane (XII)

A solution of 0.2256 g (0.67 mmol) of XII and 0.0438 g (0.19 mmol) of cetane in 23 ml of hexane was photolyzed for 40 min. The mixture was analyzed by GLC as being XIII (63% yield) and phenyl(trimethylsilyl)acetylene (6% yield). Compound XIII was isolated by preparative GLC; exact mass 336.1734 (calcd.: 336.1730); NMR (δ, ppm in C_6D_6) 0.35 (Me_3Si, s, 9H), 0.54 (MeSi, s, 3H), 2.13 (*p*-Me—C, s, 3H), 2.68 (*o*-Me—C, s, 6H), 6.78 (mesityl ring protons, s, 2H), 7.1—7.8 (phenyl ring protons, m, 5H) (Found: C, 74.62; H, 8.27. $C_{21}H_{28}Si_2$ calcd.: C, 74.93; H, 8.38%).

Reaction of silacyclopropene XIII with methanol

In a 25-ml flask was placed 0.096 g (0.29 mmol) of XIII and 0.0417 g (0.16 mmol) of octadecane dissolved in 20 ml of dry benzene under a nitrogen atmosphere. To this was added 1 ml of dry methanol. The mixture was analyzed by GLC as being methoxysilane XIV (93% yield). Compound XIV was isolated by preparative GLC; M^+ 368 (mol. wt. 368.67); IR (cm^{-1}) 1090; NMR (δ, ppm) —0.20 (Me_3Si, s, 9H), 0.41 (MeSi, s, 3H), 2.24 (*p*-Me—C, s, 3H), 2.28 (*o*-Me—C, s, 6H), 3.42 (Me—O, s, 3H), 6.38 (vinylic proton, s, 1H), 6.68 (mesityl ring protons, s, 2H), 6.8—7.2 (phenyl ring protons, m, 5H) (Found: C, 71.71; H, 8.63. $C_{22}H_{32}OSi_2$ calcd.: C, 71.67; H, 8.75%).

Thermolysis of silacyclopropenes

The following is typical of the procedures used. A mixture of 6.5 mg of II and 11.1 mg of eicosane was placed in a carefully dried glass tube (10 cm × 0.6 cm). The glass tube was sealed under vacuum, and then heated for 55 h at 250°C. GLC analysis of the reaction mixture indicated quantitative formation of I.

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References

1 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 131 (1977) C15.
2 M. Ishikawa, T. Fuchikami and M. Kumada, J. Amer. Chem. Soc., 99 (1977) 245.
3 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 190 (1980) 117.
4 R.T. Conlin and P.P. Gaspar, J. Amer. Chem. Soc., 98 (1976) 3715.
5 D. Seyferth, D.C. Annarelli and S.C. Vick, J. Amer. Chem. Soc., 98 (1976) 6382.
6 H. Sakurai, Y. Kamiyama and Y. Nakadaira, J. Amer. Chem. Soc., 99 (1977) 3879.
7 D. Seyferth, T.F.O. Lim and D.P. Duncan, J. Amer. Chem. Soc., 100 (1978) 1626.
8 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 135 (1977) C45.
9 W. Ando, M. Ikeno and A. Sekiguchi, J. Amer. Chem. Soc., 100 (1978) 3613.
10 W. Ando and M. Ikeno, Chem. Lett., (1978) 609.
11 M. Ishikawa, H. Sugisawa, T. Fuchikami and M. Kumada, to be published.
12 (a) M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 178 (1979) 105; (b) M. Ishikawa, H. Sugisawa, K. Yamamoto and M. Kumada, J. Organometal. Chem., 179 (1979) 377.
13 See Y. Nakadaira, Yuki Gosei Kagaku Kyokai Shi, 37 (1979) 732.
14 W. Atwell and J.G. Uhlmann, J. Organometal. Chem., 52 (1973) C21.
15 D. Seyferth and S.C. Vick, J. Organometal. Chem., 125 (1977) C11.
16 L.Q. Minh, J.C. Billiotte and P. Cadiot, Compt. Rend., 251 (1960) 730.
17 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., 118 (1976) 139.
18 K. Tamao and M. Kumada, J. Organometal. Chem., 30 (1971) 339.