

SILICON—CARBON UNSATURATED COMPOUNDS

XIV*. FORMATION AND REACTIONS OF 1,1,2,2-TETRATOLYL-3,4-BIS[BIS(TRIMETHYLSILYL)METHYLENE]-1,2-DISILACYCLOBUTANES

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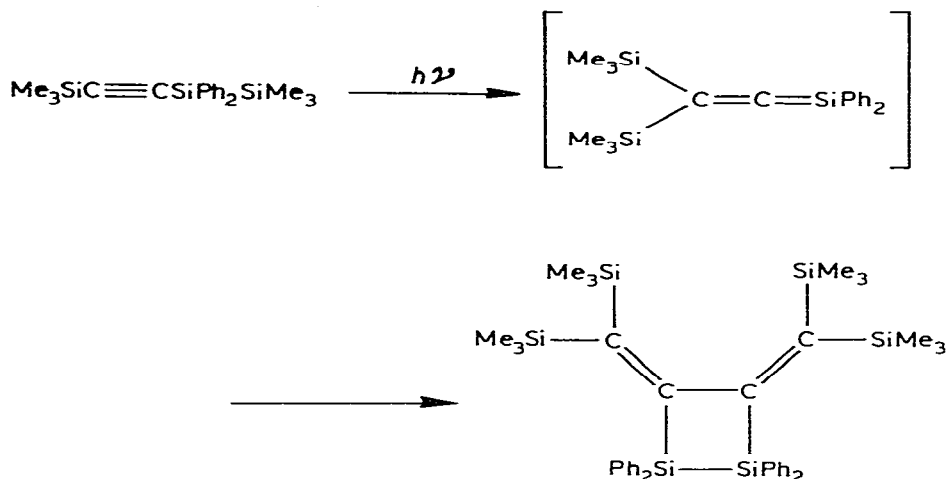
Summary

The photolysis of 1,1-di-*o*-tolyl-, 1,1-di-*m*-tolyl- and 1,1-di-*p*-tolyl-1-(trimethylsilylethynyl)trimethyldisilane gave the respective 1,1,2,2-tetratolyl-3,4-bis[(trimethylsilyl)methylene]-1,2-disilacyclobutanes. These compounds isomerized photochemically and thermally to give 1,1,2,2-tetratolyl-4,4-bis(trimethylsilyl)-3-[bis(trimethylsilyl)ethenylidene]-1,2-disilacyclobutanes in almost quantitative yield. The thermolysis of 1,1,2,2-tetra-*m*-tolyl- and 1,1,2,2-tetra-*p*-tolyl-4,4-bis(trimethylsilyl)-3-[bis(trimethylsilyl)ethenylidene]-1,2-disilacyclobutane afforded two types of the 1,3-disilacyclobutane derivative, but 1,1,2,2-tetra-*o*-tolyl-4,4-bis(trimethylsilyl)-3-[bis(trimethylsilyl)ethenylidene]-1,2-disilacyclobutane yielded 1,1,3,3-tetra-*o*-tolyl-2,4-bis[bis(trimethylsilyl)ethenylidene]-1,3-disilacyclobutane as the sole product.

Introduction

The chemistry of 1,2-disilacyclobutanes has attracted considerable interest over the past several years [1–7]. Recently, we have found that photolysis of 1,1-diphenyl-1-(trimethylsilylethynyl)trimethyldisilane affords 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane arising from head-to-head dimerization of the transiently formed silapropadiene, and reported that this 1,2-disilacyclobutane exhibits anomalous photochemical and thermal behavior [6].

* For Part XIII see ref. 6.



In order to learn much more about the chemistry of the 1,2-disilacyclobutane, we prepared three isomers of the 1,2-disilacyclobutane by the photolysis of 1,1-di-*o*-tolyl-, 1,1-di-*m*-tolyl-, and 1,1-di-*p*-tolyl-1-(trimethylsilylethynyl)trimethyldisilane and investigated some of their chemical behavior.

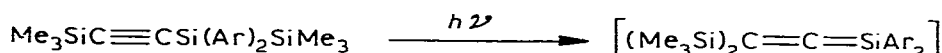
Results and discussion

Photolysis of 1,1-ditolyl-1-(trimethylsilylethynyl)trimethyldisilane

The starting compounds *o*-, *m*- and *p*-tolyl-substituted trimethylsilylethynyl-disilane were synthesized by the reaction of 1-chloro-1,1-ditolyltrimethyldisilane prepared from 1,1,1-trichlorotrimethyldisilane and the corresponding tolyl-lithium, with trimethylsilylethynyllithium in high yield.

When a benzene solution of 1,1-di-*m*-tolyl-1-(trimethylsilylethynyl)trimethyldisilane (I) was irradiated with a low-pressure mercury lamp having a Vycor filter in the absence of a trapping agent for 11 h at room temperature, a yellow crystalline compound, 1,1,2,2-tetra-*m*-tolyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane (II) arising from head-to-head dimerization of the transiently formed silapropadiene (A) was obtained in 20% yield. A higher yield (29%) of II was obtained when I was photolyzed in the presence of bis(trimethylsilyl)acetylene [6]. The formation of the head-to-head dimer seems to be a general reaction in the present photolysis. Thus, irradiation of 1,1-di-*p*-tolyl-1-(trimethylsilylethynyl)trimethyldisilane (III) with a low-pressure mercury lamp afforded 1,1,2,2-tetra-*p*-tolyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane (IV), which could readily be isolated as yellow crystals, in 21% yield. The photolysis of III in the presence of bis(trimethylsilyl)acetylene again afforded a higher yield of IV (29%). The photolysis of 1,1-di-*o*-tolyl-1-(trimethylsilylethynyl)trimethyldisilane (V) similarly gave an orange crystalline compound (VI), but the yield (ca. 3%) was extremely low. Such a low yield could not be improved by adding bis(trimethylsilyl)acetylene. Presumably, sterically bulky *o*-tolyl groups retard dimerization of the silapropadiene A.

The structures of II and IV were confirmed by mass, IR and ^1H NMR spectroscopic analyses. Compound II shows two sharp signals with equal intensities

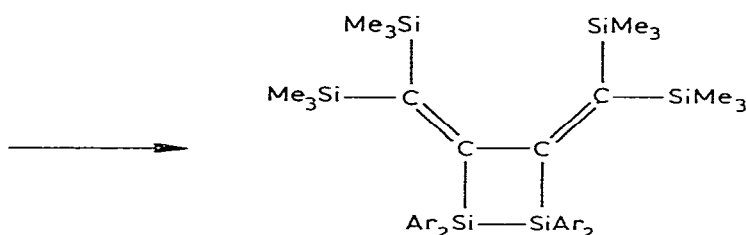


(I, Ar = *m*-tolyl ;

(A)

III, Ar = *p*-tolyl ;

V, Ar = *o*-tolyl)



(II, Ar = *m*-tolyl ;

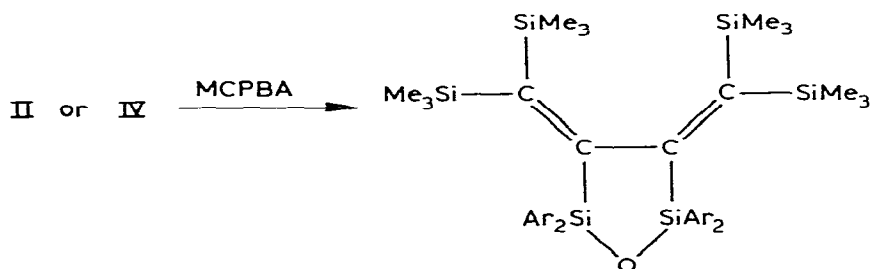
IV, Ar = *p*-tolyl ;

VI, Ar = *o*-tolyl)

at δ 0.05 and 0.48 ppm attributed to two different kinds of the methylsilyl protons and two signals at 2.02 and 2.25 ppm due to the methyl protons of the *m*-tolyl groups, along with the phenyl ring protons. The presence of two different kinds of methyl protons of the *m*-tolyl groups indicates that two *m*-tolyl groups on each silicon atom in the disilacyclobutane ring are non-equivalent. This finding is in accord with the results obtained from ^{13}C NMR spectrum of 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane indicating the presence of non-equivalent phenyl groups [6]. Similarly, compound IV exhibits two singlets in the methylsilyl region and two singlets in the methyl region of the *p*-tolyl groups. Under similar conditions, however, compound VI shows multiple resonances in the methylsilyl region and also in the methyl region of the *o*-tolyl groups. Such an anomalous spectrum for VI can be explained by hindered rotation. Indeed, upon warming the solution of VI in toluene- d_8 at 100°C, two multiplets in the methylsilyl region changed into two sharp singlets with equal intensities, while the methyl resonances of the *o*-tolyl groups changed into the complex broad multiplets.

Interestingly, no head-to-tail dimer, 1,3-disilacyclobutane, was detected in the photolysis mixture of I, III and V by spectroscopic analysis. All 1,2-disilacyclobutanes reported here are unaffected by molecular oxygen and moisture. However, compounds II and IV reacted with a strong oxidizing agent such as *m*-chloroperoxybenzoic acid (MCPBA) to afford the respective oxygen-containing five membered cyclic compounds. Thus, treatment of II with 1 mol equiv of MCPBA in methylene chloride at 0°C gave a yellow crystalline product, 2,2,5,5-tetra-*m*-tolyl-3,4-bis[bis(trimethylsilyl)methylene]-1-oxa-2,5-disilacyclopentane (VII) in 89% yield. Similar treatment of IV with MCPBA in methylene chloride gave 2,2,5,5-tetra-*p*-tolyl-3,4-bis[bis(trimethylsilyl)methylene]-1-oxa-2,5-disilacyclopentane (VIII) in 92% yield. In marked contrast to II and IV, compound VI did not react with MCPBA under identical conditions.

The starting VI was recovered unchanged quantitatively. In this case, it seems likely that the bulky *o*-tolyl groups prevent an approach of the MCPBA molecule to the silicon-silicon bond in the disilacyclobutane ring.

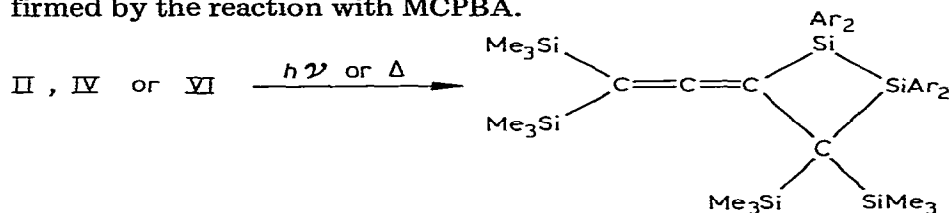


(VII, Ar = *m*-tolyl;

VIII, Ar = *p*-tolyl)

Isomerization of 1,2-disilacyclobutanes II, IV and VI

Like 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane reported previously [6], compound II undergoes isomerization photochemically to give another type of 1,2-disilacyclobutane, which seems to be a general reaction for 1,1,2,2-tetraaryl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutanes. When compound II was irradiated with a high-pressure mercury lamp having a Pyrex filter in benzene for 10 h, 1,1,2,2-tetra-*m*-tolyl-4,4-bis(trimethylsilyl)-3-[bis(trimethylsilyl)ethenylidene]-1,2-disilacyclobutane (IX) was obtained in 90% yield, in addition to 10% of unchanged II. Similar irradiation of IV in benzene for 10 h yielded 1,2-disilacyclobutane (X) in excellent yield. Irradiation of VI under the same conditions, however, gave isomer (XI) in only 25% yield, and 75% of the starting VI was recovered unchanged. The isomerization of compounds II, IV and VI to the respective ethenylidene-1,2-disilacyclobutanes also occurred thermally. Heating II at 200°C for 1.5 h in a sealed tube gave IX in 98% yield. Similarly, X was obtained in 97% yield from the thermolysis of IV. Compound VI is thermally more stable than II and IV. When VI was heated at 200°C for 1.5 h in a sealed glass tube, a small amount of XI (ca. 10%), together with the starting VI (ca. 90%), was detected by ¹H NMR spectroscopic analysis of the reaction mixture. Prolonged heating of VI at 200°C, however, gave XI in almost quantitative yield. That compounds IX and X contain the silicon-silicon bond in the four-membered ring was confirmed by the reaction with MCPBA.

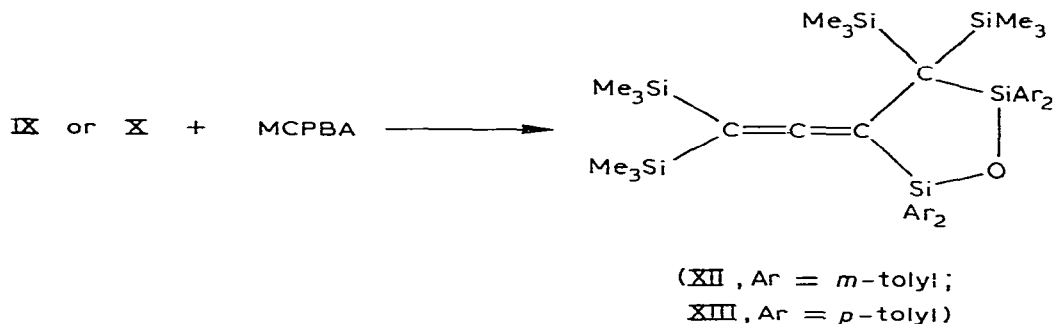


(IX, Ar = *m*-tolyl;

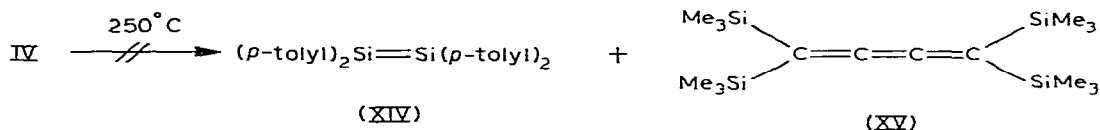
X, Ar = *p*-tolyl;

XI, Ar = *o*-tolyl)

Thus, the reaction of IX with MCPBA in methylene chloride at 0°C gave cyclic siloxane (XII) in 87% yield, while X reacted with MCPBA to give product (XIII) in 91% yield. Again, compound XI did not react with MCPBA under the same conditions, the starting XI being recovered unchanged.



The fact that the thermolysis of IV in the presence of anthracene at 200°C afforded X in almost quantitative yield, but neither adduct arising from the reaction of anthracene with tetra-*p*-tolylidisilene (XIV) nor 1,1,4,4-tetrakis-(trimethylsilyl)butatriene (XV) was detected by spectroscopic analysis, strongly suggests that the isomerization of II, IV and VI to IX, X and XI, respectively, proceeds via a concerted 1,3-shift of the disilanyl group.



Thermolysis of IX, X and XI

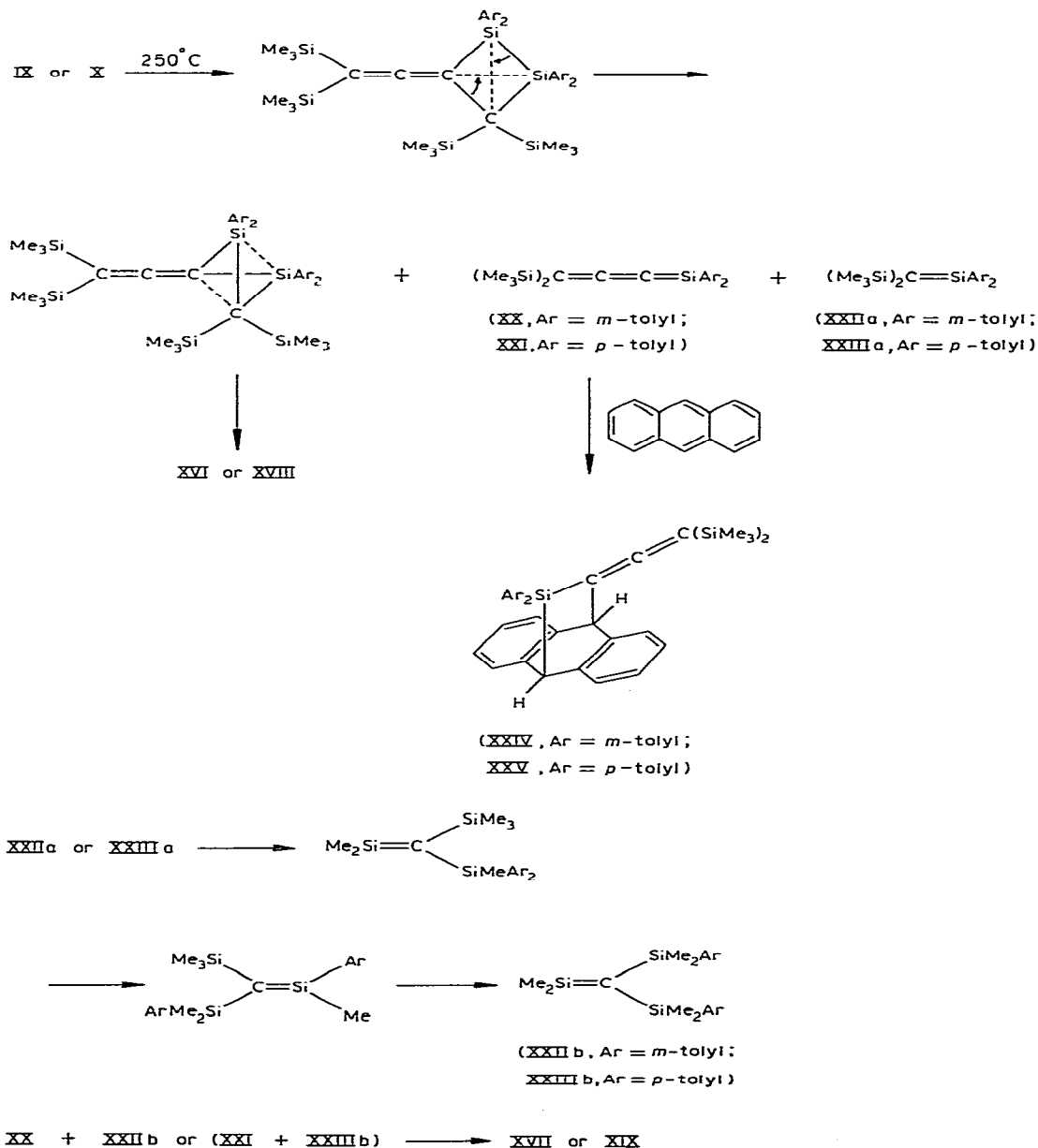
Compounds IX and X are stable at 200°C in a sealed tube; however, at higher temperature, they undergo further isomerization giving two types of the respective 1,3-disilacyclobutane. Thus, heating IX at 250°C for 3 h in a sealed glass tube afforded a 1/1 mixture of two isomers, 1,1,3,3-tetra-*m*-tolyl-2-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,3-disilacyclobutane (XVI) and 1,1-dimethyl-3,3-di-*m*-tolyl-2-[bis(trimethylsilyl)ethenylidene]-4,4-bis(*m*-tolyltrimethylsilyl)-1,3-disilacyclobutane (XVII) in almost quantitative yield. All attempts to separate XVII from XVI were unsuccessful. Treatment of a mixture consisting of XVI and XVII with preparative TLC afforded only XVI, while compound XVII decomposed to give a nonvolatile product on silica gel. Fractional recrystallization of the mixture gave XVI in a pure form, but pure XVII could not be obtained. Compound XVII thus isolated was always contaminated with a small amount of XVI (ca. 15%). Thermolysis of X again led to the formation of a 1/1 mixture of 1,3-disilacyclobutanes (XVIII) and (XIX).

The structures of XVII and XIX were identified by mass, IR and ¹H NMR spectroscopic methods. A strong band at 1880 cm⁻¹ in the IR spectrum of XVII clearly indicates that it must have an allenic structure. Compound XIX also showed this band at 1880 cm⁻¹. The ¹H NMR spectrum of XVII revealed six resonances with relative intensities of 3/3/9/3/6 at δ -0.32, 0.08, 0.17, 0.67, 2.36 and 7.00–8.00, attributed to Me₂Si, Me₂Si, Me₃Si, Me₂Si, *m*-MeC

and phenyl ring protons, respectively. As expected, XIX also showed four singlets attributed to four kinds of the methylsilyl protons, as well as a broad singlet and multiplet signals due to the methyl protons of the *p*-tolyl groups and the phenyl ring protons, respectively.

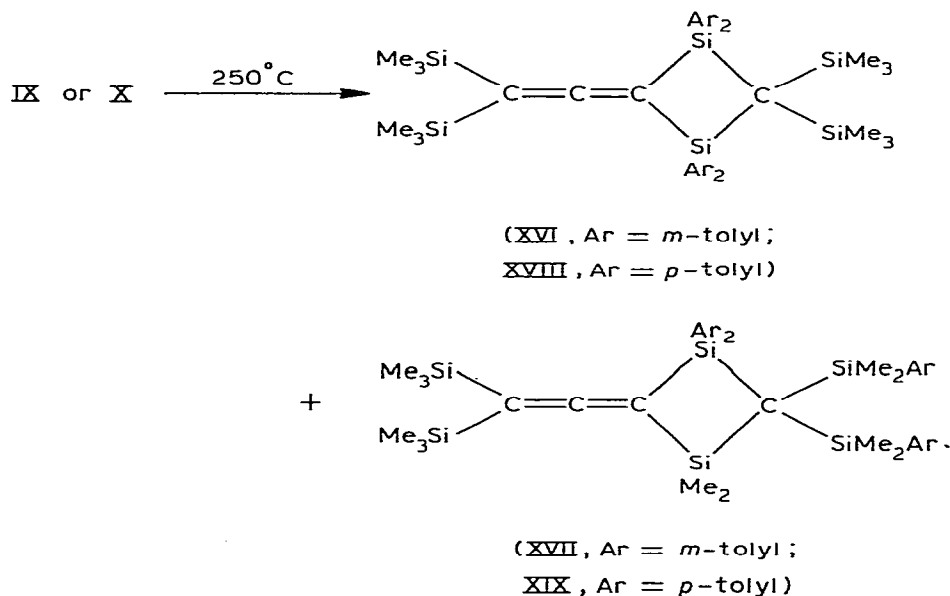
Such anomalous isomerization of the 1,2-disilacyclobutane has already been found in the thermolysis of 1,1,2,2-tetraphenyl-4,4-bis(trimethylsilyl)-3-[bis-

SCHEME 1



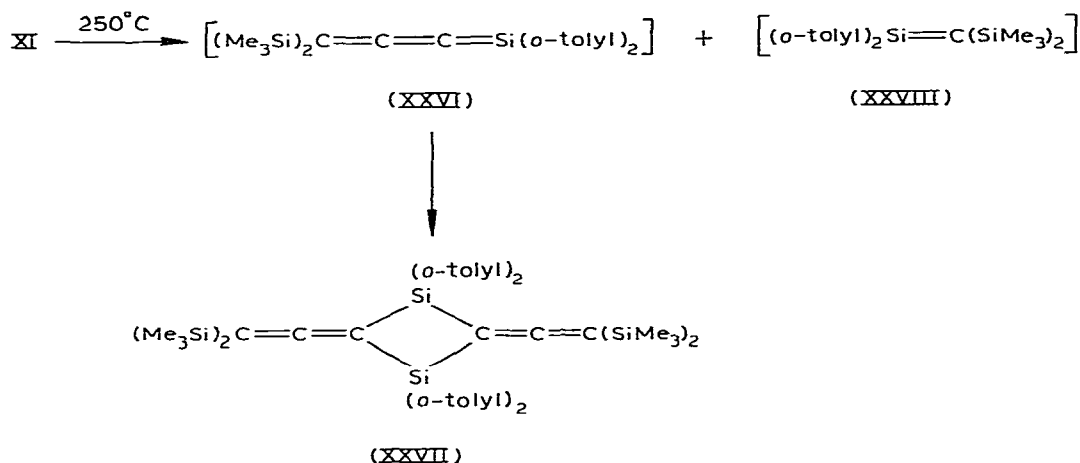
(trimethylsilyl)ethenylidene]-1,2-disilacyclobutane. The structure of the isomerization product, 1,1-dimethyl-3,3-diphenyl-4,4-bis(phenyldimethylsilyl)-2-[bis(trimethylsilyl)ethenylidene]-1,3-disilacyclobutane, analogous to XVII and XIX, was verified by an X-ray diffraction study [6].

When IX was heated at 250°C in the presence of anthracene, compound XVI was obtained in 39% yield, along with 41% of adduct (XXIV) produced from the reaction of anthracene with 1,1-di-*m*-tolyl-4,4-bis(trimethylsilyl)-1-silabutatriene (XX) (see Scheme 1). Neither 1,3-disilacyclobutane XVII nor product resulting from the reaction of 1,1-di-*m*-tolylbis(trimethylsilyl)-1-silaethene (XXIIa) with anthracene was detected either by TLC analysis or spectroscopic analysis.

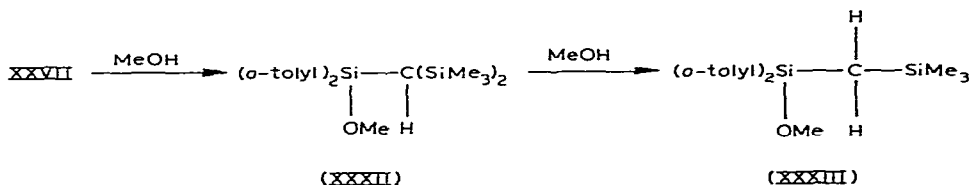
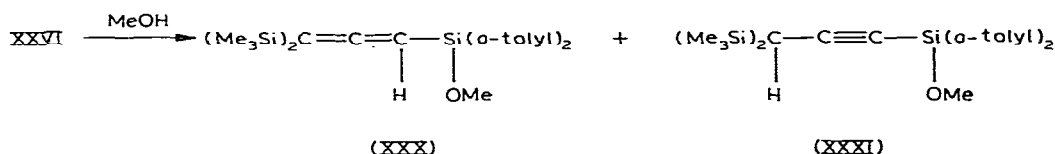
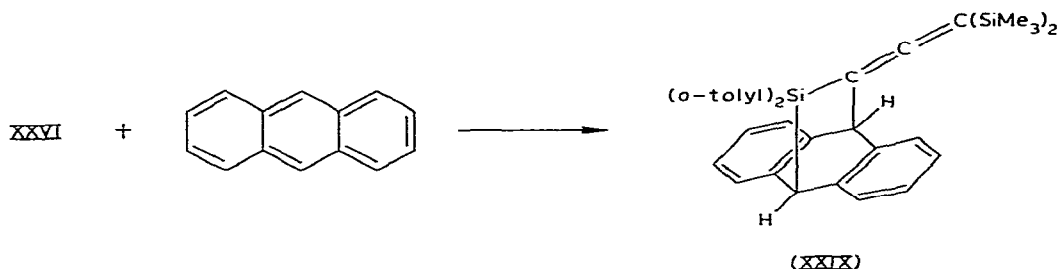


These results indicate that thermolysis of IX proceeds by two different routes. One involves a concerted 1,3-silyl shift leading to the 1,3-disilacyclobutane XVI, and the other comprises the formation of two reactive intermediates XX and XXIIa. In the absence of a trapping agent, intermediate XXIIa thus formed presumably isomerizes to give another intermediate (XXIIb) [8], which can react with XX yielding XVII as shown in Scheme 1. When compound X was thermolyzed in the presence of anthracene under similar conditions, compound XVIII and anthracene adduct (XXV) were obtained in 42 and 44% yield, respectively. Again, silaethene intermediate XXIIIa was transformed into nonvolatile substances.

In marked contrast to the thermolysis of IX and X, compound XI afforded no 1,3-disilacyclobutanes analogous to XVI and XVII. Thus, when XI was heated at 250°C for 4 h, compound XXVII was obtained in 48% yield as the sole volatile product. The formation of XXVII may be best explained in terms of dimerization of 1,1-di-*o*-tolyl-4,4-bis(trimethylsilyl)-1-silabutatriene intermediate (XXVI). In fact, intermediate XXVI could be trapped by the quench-



ing reaction using anthracene. Thus, heating XI at 250°C with anthracene afforded an anthracene-butatriene adduct (XXIX) in 44% yield. Once again, no volatile product to be expected to form from 1,1-di-*o*-tolylbis(trimethylsilyl)-1-silaethene (XXVIII) was found by spectroscopic analysis. However, when XI was heated at 250°C in the presence of methanol for 4 h, the intermediate XXVIII could be trapped by methanol. In this thermolysis, four products, 1-di-



o-tolylmethoxysilyl-3,3-bis(trimethylsilyl)propadiene (XXX), 1-di-*o*-tolylmethoxysilyl-3,3-bis(trimethylsilyl)propyne (XXXI), bis(trimethylsilyl)methyl-di-*o*-tolylmethoxysilane (XXXII) and trimethylsilylmethyl-di-*o*-tolylmethoxy-

silane (XXXIII) were obtained in 20, 30, 39 and 11% yield, respectively. The formation of XXX and XXXI may be understood in terms of the intermediate XXVI undergoing methanol addition in a 1,2 and 1,4 fashion, respectively. Compound XXXII can be rationalized by addition of methanol to a silicon-carbon double bond in the intermediate XXVIII, while XXXIII by further reaction of XXXI with methanol.

The structures of new compounds described here were based on mass, IR and ^1H NMR spectroscopic analysis (see Experimental).

Experimental

General procedure

Infrared spectra were obtained with the use of a Hitachi Model EPI-G3 Grating infrared spectrometer. ^1H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer in carbon tetrachloride with the use of cyclohexane as an internal standard. Mass spectra were measured on a JEOL Model JMS-D300 mass spectrometer equipped with a JMA-2000 data processing system. Preparative thin layer chromatography was carried out with the use of silica gel 60 PF₂₅₄ UV indicating gel.

Preparation of 1,1-di-*o*-tolyl-, 1,1-di-*m*-tolyl- and 1,1-di-*p*-tolyl-1-(trimethylsilylethynyl)trimethyldisilane

The following is typical of the procedures used. In a 300 ml of three-necked flask fitted with a stirrer, reflux condenser and dropping funnel was placed 15.0 g (0.072 mol) of 1,1,1-trichlorotrimethyldisilane [9] in 100 ml of dry ether. To this was added *o*-tolyllithium/ether solution prepared from 27.2 g (0.159 mol) of *o*-bromotoluene and 3.34 g (0.477 g-atom) of lithium metal in 100 ml of ether with ice cooling. After the mixture was stirred at room temperature for 1 h, trimethylsilylethynyllithium prepared from 9.2 g (0.094 mol) of trimethylsilylacetylene and 53 ml of butyllithium/hexane solution (1.6 M) at -70°C was added to the mixture at room temperature. The reaction mixture was then refluxed for 3 h and the mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over potassium carbonate. Distillation gave 22.1 g (80% yield) of V, b.p. $147-149^\circ\text{C}/1.0$ Torr, m.p. 69°C (after recrystallization from ethanol); M^+ 380 (mol. wt. 380.76); IR (cm^{-1}) 2100, 1450, 1250, 850; ^1H NMR (δ , ppm) 0.23 (Me_3Si , s, 9H), 0.26 (Me_3Si , s, 9H), 2.20 (*o*-MeC, s, 6H), 6.95–7.70 (ring protons, m, 8H) (Found: C, 69.13; H, 8.19. $\text{C}_{22}\text{H}_{32}\text{Si}_3$ calcd.: C, 69.40; H, 8.47%). For I (70% yield), b.p. $132^\circ\text{C}/0.4$ Torr, M^+ 380 (mol. wt. 380.76); IR (cm^{-1}) 2100, 1460, 1400, 1250, 1110, 840; ^1H NMR (δ , ppm) 0.20 (Me_3Si , s, 9H), 0.26 (Me_3Si , s, 9H), 2.35 (*m*-MeC, s, 6H), 7.00–7.40 (ring protons, m, 8H) (Found: C, 69.67; H, 8.48. $\text{C}_{22}\text{H}_{32}\text{Si}_3$ calcd.: C, 69.40; H, 8.47%). For III (80% yield), b.p. $143^\circ\text{C}/0.2$ Torr, M^+ 380 (mol. wt. 380.76); IR (cm^{-1}) 2100, 1445, 1390, 1250, 850; ^1H NMR (δ , ppm) 0.20 (Me_3Si , s, 9H), 0.26 (Me_3Si , s, 9H), 2.32 (*p*-MeC, s, 6H), 7.10 (ring protons, d, 4H, J 8 Hz), 7.44 (ring protons, d, 4H, J 8 Hz) (Found: C, 69.16; H, 8.55. $\text{C}_{22}\text{H}_{32}\text{Si}_3$ calcd.: C, 69.40; H, 8.47%).

Preparation of 1,2-disilacyclobutanes II, IV and VI

The following is typical of the procedures used. In a 500 ml reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed 4.0101 g (1.05×10^{-1} mol) of I in ca. 500 ml of dry benzene. The solution was irradiated at room temperature for 11 h with a slow stream of nitrogen bubbling through the mixture. After evaporation of the solvent under reduced pressure, yellow crystals were obtained. Recrystallization of the crystals from hexane afforded 0.8163 g (20% yield) of II, m.p. 188–189°C (dec.); M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1470, 1440, 1395, 1260, 1245, 1110, 910, 830; ^1H NMR (δ , ppm) –0.15 (Me_3Si , s, 18H), 0.29 (Me_3Si , s, 18H), 1.95 (*m*-MeC, s, 6H), 2.30 (*m*-MeC, s, 6H), 6.50–7.60 (ring protons, m, 16H) (Found: C, 69.40; H, 8.59. $\text{C}_{44}\text{H}_{64}\text{Si}_6$ calcd.: C, 69.40; H, 8.47%). For IV (21% yield), m.p. 225°C (dec.); M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1440, 1260, 1240, 1100, 915, 830; ^1H NMR (δ , ppm) –0.18 (Me_3Si , s, 18H), 0.28 (Me_3Si , s, 18H), 2.24 (*p*-MeC, s, 6H), 2.44 (*p*-MeC, s, 6H), 6.75 (ring protons, d, 4 H, *J* 8 Hz), 6.88 (ring protons, d, 4 H, *J* 8 Hz), 7.13 (ring protons, d, 4H, *J* 8 Hz), 7.55 (ring protons, d, 4H, *J* 8 Hz) (Found: C, 69.64; H, 8.47. $\text{C}_{44}\text{H}_{64}\text{Si}_5$ calcd.: C, 69.40; H, 8.47%). For VI (3% yield), m.p. 249°C (dec.); M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1440, 1260, 1245, 1120, 910, 845; ^1H NMR (δ , ppm) –0.18, 0.12 (Me_3Si , 18H), 0.30, 0.32, 0.33 (shoulder) (Me_3Si , 18H), 1.75–2.24 (*o*-MeC, m, 12H), 6.14–8.12 (ring protons, m, 16H) (Found: C, 68.96; H, 8.65. $\text{C}_{44}\text{H}_{64}\text{Si}_6$ calcd.: C, 69.40; H, 8.47%).

Photolysis of I in the presence of bis(trimethylsilyl)acetylene

A mixture of 1.1937 g (3.14×10^{-3} mol) of I and 3.0209 g (17.7×10^{-3} mol) of bis(trimethylsilyl)acetylene in 80 ml of dry benzene was irradiated for 5 h at room temperature. After the usual workup, 0.3512 g (29% yield) of II was obtained.

Reaction of II with MCPBA

To a solution of 34.1 mg (4.48×10^{-5} mol) of II in 2 ml of methylene chloride in a 5 ml test tube was added 10.8 mg (6.26×10^{-5} mol) of MCPBA dissolved in 1 ml of methylene chloride at 0°C. The reaction mixture was concentrated to give crude VII. Pure VII (31.0 mg, 89% yield) was isolated by preparative TLC, m.p. 185°C; M^+ 776 (mol. wt. 777.52); IR (cm^{-1}) 1475, 1445, 1395, 1260, 1245, 1225, 1115, 935, 840; ^1H NMR (δ , ppm) 0.03 (Me_3Si , s, 18H), 0.04 (Me_3Si , s, 18H), 2.27 (*m*-MeC, s, 6H), 2.35 (*m*-MeC, s, 6H), 7.05–7.75 (ring protons, m, 16H) (Found: C, 67.93; H, 8.02. $\text{C}_{44}\text{H}_{64}\text{OSi}_6$ calcd.: C, 67.97; H, 8.30%).

Reaction of IV with MCPBA

To a solution of 59.5 mg (7.81×10^{-5} mol) of IV in 2 ml of methylene chloride was added 18.4 mg (1.07×10^{-4} mol) of MCPBA in 1 ml of methylene chloride at 0°C. After the usual workup, 55.7 mg (92% yield) of VIII was obtained. M.p. 257–157.5°C; M^+ 776 (mol. wt. 777.52); IR (cm^{-1}) 1440, 1260, 1245, 1110, 935, 845; ^1H NMR (δ , ppm) 0.00 (Me_3Si , s, 18H), 0.04 (Me_3Si , s, 18H), 2.35 (*p*-MeC, s, 6H), 2.44 (*p*-MeC, s, 6H), 7.01 (ring protons, d, 4H, *J* 8 Hz), 7.06 (ring protons, d, 4H, *J* 8 Hz), 7.36 (ring protons, d, 4H, *J* 8 Hz),

7.76 (ring protons, d, 4H, J 8 Hz) (Found: C, 68.17; H, 8.49. $C_{44}H_{64}OSi_6$ calcd.: C, 67.97; H, 8.30%).

Photoisomerization of II

Compound II (13.7 mg, 1.80×10^{-5} mol) in 1 ml of dry benzene was placed in a Pyrex NMR tube. The solution was deoxygenated by bubbling dry argon and the tube was sealed with a serum cup. It was then irradiated externally with a high-pressure mercury lamp with a quartz filter for 10 h. The 1H NMR spectrum of the reaction mixture showed the presence of IX (90% yield), along with 10% of the starting II.

Photoisomerization of IV and VI

In a Pyrex NMR tube was placed a solution of 17.1 mg (2.25×10^{-5} mol) of IV in 1 ml of benzene. After 10 h irradiation, the 1H NMR spectroscopic analysis of the mixture showed the formation of X (90% yield) and the presence of 10% of the starting IV. Similar irradiation of VI for 10 h afforded XI in 25% yield, in addition to 75% of the starting VI.

Thermolysis of II

In a glass tube previously flushed with argon was placed 112.9 mg (1.48×10^{-4} mol) of II. The glass tube was purged with dry argon and then sealed. The tube was heated at 200°C for 1.5 h. Upon cooling the resulting product to room temperature, white crystals were obtained. They were collected to give 110.5 mg (98% yield) of IX. Recrystallization from hexane gave IX as colorless crystals, m.p. 176°C; M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1855, 1395, 1260, 1245, 1110, 845; 1H NMR (δ , ppm) 0.03 (Me_3Si , s, 18H), 0.06 (Me_3Si , s, 18H), 2.15 ($m-MeC$, s, 6H), 2.32 ($m-MeC$, s, 6H), 7.00–7.65 (ring protons, m, 16H) (Found: C, 69.10; H, 8.33. $C_{44}H_{64}Si_6$ calcd.: C, 69.40; H, 8.47%).

Thermolysis of IV

Compound IV (100 mg, 1.31×10^{-4} mol) was heated at 200°C for 1.5 h in a sealed glass tube. It was cooled down to room temperature to give 97.3 mg (97% yield) of X as colorless crystals. M.p. 196–197°C (after recrystallization from hexane), M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1885, 1440, 1245, 1095, 845; 1H NMR (δ , ppm) 0.05 (Me_3Si , s, 18H), 0.10 (Me_3Si , s, 18H), 2.29 ($p-MeC$, s, 6H), 2.38 ($p-MeC$, s, 6H), 6.92 (ring protons, d, 4H, J 8 Hz), 7.09 (ring protons, d, 4H, J 8 Hz), 7.38 (ring protons, d, 4H, J 8 Hz), 7.50 (ring protons, d, 4H, J 8 Hz) (Found: C, 69.15; H, 8.71. $C_{44}H_{64}Si_6$ calcd.: C, 69.40; H, 8.47%).

Thermolysis of IV in the presence of anthracene

A mixture of 107.4 mg (1.40×10^{-4} mol) of IV and 46.2 mg (2.6×10^{-4} mol) of anthracene was heated at 200°C for 15 h in a sealed tube. The 1H NMR spectrum of the mixture showed the presence of X in quantitative yield.

Thermolysis of VI

Compound VI (97 mg, 1.27×10^{-4} mol) was heated at 250°C for 1 h in a sealed glass tube. The 1H NMR spectrum of the reaction product showed the

presence of 100% of XI. Recrystallization of XI from ethanol gave XI as colorless crystals. M.p. 257°C; M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1840, 1440, 1245, 835; ^1H NMR (δ , ppm) 0.10 (Me_3Si , s, 18H), 0.19 (Me_3Si , s, 18H), 1.92 (*o*-MeC, s, 6H), 1.97 (*o*-MeC, s, 6H), 6.80–7.95 (ring protons, m, 16H) (Found: C, 69.32; H, 8.26. $\text{C}_{44}\text{H}_{64}\text{Si}_6$ calcd.: C, 69.40; H, 8.47%).

Reaction of IX with MCPBA

To a solution of 35.5 mg (4.66×10^{-5} mol) of IX in 2 ml of methylene chloride was added 10.0 mg (5.79×10^{-5} mol) of MCPBA dissolved in 1 ml of methylene chloride at 0°C. The reaction mixture was concentrated and chromatographed by preparative TLC to give 31.0 mg (87% yield) of cyclic siloxane XII. M.p. 192°C (after recrystallization from ethanol); M^+ 776 (mol. wt. 777.52); IR (cm^{-1}) 1865, 1830, 1445, 1400, 1250, 1115, 940, 835; ^1H NMR (δ , ppm) 0.00 (Me_3Si , s, 18H), 0.02 (Me_3Si , s, 18H), 2.19 (*m*-MeC, s, 6H), 2.36 (*m*-MeC, s, 6H), 7.00–7.70 (ring protons, m, 16H) (Found: C, 67.78; H, 8.15. $\text{C}_{44}\text{H}_{64}\text{OSi}_6$ calcd.: C, 67.97; H, 8.30%).

Reaction of X with MCPBA

To a solution of 96.2 mg (1.26×10^{-4} mol) of X in 2 ml of methylene chloride was added 25.2 mg (1.46×10^{-4} mol) of MCPBA in 1 ml of methylene chloride at 0°C. The reaction mixture was concentrated and chromatographed by preparative TLC to give 89.3 mg (91% yield) of XIII. M.p. 206–208°C (after recrystallization from ethanol); M^+ 776 (mol. wt. 777.52); IR (cm^{-1}) 1865, 1830, 1390, 1250, 1105, 870, 840; ^1H NMR (δ , ppm) 0.03 (Me_3Si , s, 36H), 2.29 (*p*-MeC, s, 6H), 2.37 (*p*-MeC, s, 6H), 7.35 (ring protons, d, 4H, J 8 Hz), 7.50 (ring protons, d, 4H, J 8 Hz), 7.91 (ring protons, d, 4H, J 8 Hz), 7.95 (ring protons, d, 4H, J 8 Hz) (Found: C, 68.11; H, 8.47. $\text{C}_{44}\text{H}_{64}\text{OSi}_6$ calcd.: C, 67.97; H, 8.30%).

Thermolysis of IX

Compound IX (129.8 mg, 1.70×10^{-4} mol) was heated at 250°C for 3 h in a degassed sealed tube. It was cooled down to room temperature to give white crystals. The ^1H NMR spectrum of the mixture showed the presence of a 1/1 mixture of XVI and XVII in quantitative yield. Crystallization of the mixture from ethanol afforded 41.7 mg (32% yield) of XVI and 45.4 mg of XVII contaminated with 15% of XVI. For XVI, m.p. 194°C; M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1875, 1395, 1265, 1250, 1115, 840; ^1H NMR (δ , ppm) –0.19 (Me_3Si , s, 18H), 0.25 (Me_3Si , s, 18H), 2.35 (*m*-MeC, s, 12H), 7.10–8.00 (ring protons, m, 16H) (Found: C, 69.18; H, 8.51. $\text{C}_{44}\text{H}_{64}\text{Si}_6$ calcd.: C, 69.40; H, 8.47%). For XVII, M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1880, 1445, 1395, 1260, 1250, 1110, 840; ^1H NMR (δ , ppm) –0.32 (Me_2Si , s, 6H), 0.08 (Me_2Si , s, 6H), 0.17 (Me_3Si , s, 18H), 0.67 (Me_2Si , s, 6H), 2.36 (*m*-MeC, bs, 12H), 7.00–8.00 (ring protons, m, 16H).

Thermolysis of X

Compound X (91.9 mg, 1.21×10^{-4} mol) was heated at 250°C for 3 h in a degassed sealed tube. The ^1H NMR spectrum of the mixture showed the presence of a 1/1 mixture of XVIII and XIX in quantitative yield. After recrystalli-

zation from ethanol, 28.0 mg (30% yield) of pure XVIII and 36.2 mg of XIX contaminated with 15% of XVIII were obtained. For XVIII, m.p. 251–252.5°C; M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1885, 1390, 1260, 1250, 1095, 845; ^1H NMR (δ , ppm) –0.14 (Me_3Si , s, 18H), 0.28 (Me_3Si , s, 18H), 2.34 (*p*-MeC, bs, 12H), 7.02 (ring protons, d, 8H, J 8 Hz), 7.65 (ring protons, d, 8H, J 8 Hz) (Found: C, 69.41; H, 8.67. $\text{C}_{44}\text{H}_{64}\text{Si}_6$ calcd.: C, 69.40; H, 8.47%). For XIX, M^+ 760 (mol. wt. 761.52); IR (cm^{-1}) 1880, 1400, 1250, 1105, 855; ^1H NMR (δ , ppm) –0.26 (Me_2Si , s, 6H), 0.08 (Me_2Si , s, 6H), 0.23 (Me_3Si , s, 18H), 0.70 (Me_2Si , s, 6H), 2.35 (*p*-MeC, bs, 12H), 6.90–7.70 (ring protons, m, 16H).

Thermolysis of IX in the presence of anthracene

A mixture of 95.4 mg (1.25×10^{-4} mol) of IX and 62.8 mg (3.52×10^{-4} mol) of anthracene was heated at 250°C for 3 h in a sealed tube. The reaction mixture was chromatographed by preparative TLC to give 28.0 mg (39% yield) of XVI and 39.4 mg (41% yield) of anthracene adduct XXIV. For XXIV, IR (cm^{-1}) 1895, 1460, 1245, 1115, 895, 840; ^1H NMR (δ , ppm) –0.14 (Me_3Si , s, 18H), 2.17 (*m*-MeC, s, 6H), 4.37 (H–CSi, s, 1H), 4.89 (H–CSi, s, 1H), 6.80–7.70 (ring protons, m, 16H). Exact mass: 570.2605 ($\text{C}_{37}\text{H}_{42}\text{Si}_3$ calcd.: 570.2594).

Thermolysis of X in the presence of anthracene

A mixture of 79.3 mg (1.04×10^{-4} mol) of XVIII and 95.4 mg (5.35×10^{-4} mol) of anthracene was heated at 250°C for 3 h in a sealed tube. The mixture was chromatographed by TLC to give 34.5 mg (44% yield) of XVIII and 25.0 mg (42% yield) of XIV. For XXV, IR (cm^{-1}) 1895, 1250, 1110, 1100, 900, 860, 845; ^1H NMR (δ , ppm) –0.10 (Me_3Si , s, 18H), 2.26 (*p*-MeC, s, 6H), 4.25 (H–CSi, s, 1H), 4.75 (H–CSi, s, 1H), 6.80–7.20 (ring protons, m, 16H). Exact mass: 570.2568 ($\text{C}_{37}\text{H}_{42}\text{Si}_3$ calcd.: 570.2594).

Thermolysis of XI

Compound XI (49.0 mg, 6.43×10^{-5} mol) was heated at 250°C for 4 h in a degassed sealed tube. The reaction mixture was chromatographed by preparative TLC to give 12.1 mg (48% yield) of XXVII. M^+ 784 (mol. wt. 785.51); IR (cm^{-1}) 1880, 1440, 1260, 1250, 1125, 1070, 890, 840; ^1H NMR (δ , ppm) –0.01 (Me_3Si , s, 36H), 2.15 (*o*-MeC, s, 12H), 6.95–7.65 (ring protons, m, 16H) (Found: C, 70.13; H, 8.32. $\text{C}_{46}\text{H}_{64}\text{Si}_6$ calcd.: C, 70.34; H, 8.21%).

Thermolysis of XI in the presence of anthracene

A mixture of 22.1 mg (2.90×10^{-5} mol) of XI and 21.7 mg (1.22×10^{-4} mol) of anthracene was heated at 250°C for 4 h in a sealed glass tube. The mixture was chromatographed by TLC to give 5.0 mg (44% yield) of XXIX. IR (cm^{-1}) 1900, 1470, 1130, 1075, 900; ^1H NMR (δ , ppm) –0.10 (Me_3Si , s, 18H), 2.00 (*o*-MeC, s, 6H), 4.44 (H–CSi, s, 1H), 4.74 (H–CSi, s, 1H), 6.75–7.40 (ring protons, m, 16H). Exact mass: 570.2576 ($\text{C}_{37}\text{H}_{42}\text{Si}_3$ calcd.: 570.2594).

Thermolysis of XI in the presence of methanol

A mixture of 58.0 mg (7.6×10^{-5} mol) of XI and 50 μl (39 mg, 1.2×10^{-3}

mol) of methanol was heated at 250°C for 4 h in a sealed tube. The yields of products XXX, XXXI, XXXII and XXXIII were determined to be 20, 30, 39 and 11% by GLC analysis and by ^1H NMR spectroscopic analysis. A mixture of XXX and XXXI, and XXXII and XXXIII were separated by preparative GLC. For XXX, IR (cm^{-1}) 1890; ^1H NMR (δ , ppm) 0.16 (Me_3Si , s, 18H), 2.25 (*o*-MeC, s, 6H), 3.52 (MeO, s, 3H), 4.36 (H—CSi, s, 1H), 6.9—7.8 (ring protons, m). Exact mass: 424.2067 ($\text{C}_{24}\text{H}_{36}\text{OSi}_3$ calcd.: 424.2074). For XXXI, IR (cm^{-1}) 2140; ^1H NMR (δ , ppm) 0.00 (Me_3Si and HCSi_2 , s, 19H), 2.16 (*o*-MeC, s, 6H), 3.42 (MeO, s, 3H), 6.9—7.8 (ring protons, m). For XXXII, IR (cm^{-1}) 1240, 1180, 1125, 1075, 1000; ^1H NMR (δ , ppm) 0.04 (Me_3Si , s, 18H), 0.10 (HCSi_2 , s, 1H), 2.06 (*o*-MeC, s, 6H), 3.60 (MeO, s, 3H), 6.8—7.6 (ring protons, m, 8H). Exact mass: 385.1847 ($\text{C}_{22}\text{H}_{36}\text{OSi}_3$ calcd.: 385.1839). For XXXIII, IR (cm^{-1}) 1240, 1120, 1070, 1040, 1030; ^1H NMR (δ , ppm) -0.14 (Me_3Si , s, 9H), 0.44 (H_2C , s, 2H), 2.12 (*o*-MeC, s, 6H), 3.36 (MeO, s, 3H), 6.8—7.7 (ring protons, m, 8H). Exact mass: 313.1447 ($\text{C}_{19}\text{H}_{28}\text{OSi}_2$ calcd.: 313.1444).

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