# Photochemical Reactions of 1,3-Disilacyclobutane

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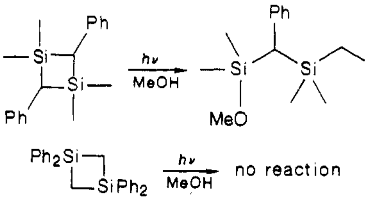
Photolysis of pure *trans*- or *cis*-1,1,3,3-tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane gives rapid isomerization to a 70/30 equilibrium mixture of the isomers and less rapid formation of ring-opened vinylsilane isomers. In the presence of MeOH, $MeOSiMe_3$, or $(EtO)_3SiH$ as traps the expected adducts to 1,1-diphenyl-2-neopentylsilene are also observed. Solvent dependence of the yields suggests that all of the products arise from singlet excited state(s). The results are consistent with the initial formation of a singlet ring-opened 1,4-biradical which recloses rapidly to starting material or goes on to the observed products.

## Introduction

The photochemical reactions of monosilacyclobutanes has been the subject of several studies.[4-6] Depending on the ring substituents the formation of silene,[4-11] silylene,[7,8] and biradical[9,10] intermediates has been observed. Thus the photolysis of 2-phenylsilacyclobutanes gave biradical intermediates[9,10] while 1,1-diphenylsilacyclobutane gave silene intermediates.[5] Photolysis of 1,2-disilacyclobutanes gave rise to both silene and silylene intermediates.[11] It is generally held that 1,3-disilacyclobutanes are not suitable silene precursors because of the unfavorable energetics leading to two silenes.[12] To our knowledge, the only photochemical study of 1,3-disilacyclobutanes as potential silene precursors has been reported by Jutzi.[10] The photolysis of a mixture of *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane in methanol gave the methanol adduct to the ring-opened 1,4-biradical as the only isolated product. However, 1,1,3,3-tetraphenyl-1,3-disilacyclobutane gave no apparent reaction under the same conditions.[10] The seeming conflict of these reports prompted us to investigate the photochemical behavior of *trans*- and *cis*-1,1,3,3-tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane, **1a**, and **1b**, respectively.



## Results and Discussion

Compounds **1a** and **1b** were prepared by a previously reported method.[13,14] Their photochemical behavior in the absence of a trap is summarized in Table I. The photolysis of a benzene or cyclohexane solution of either pure **1a** or **1b** gives a relatively rapid isomerization to an equilibrium mixture consisting of about 70% **1a** and 30% **1b**. Continued photolysis results in the decomposition of

**Table I. Photochemical Behavior of 1 in the Absence of Trapping Agents**[a]

| time, h | 1a | 1b | % 1[b] | % 2[c] | 2a/2b |
|---|---|---|---|---|---|
| 0 | 93 | 7 | 100 | | |
| 6 | 71 | 29 | 61 | 39 | 2.00 |
| 8 | 70 | 30 | 35 | 44 | 1.59 |
| 10 | 70 | 30 | 25 | 50 | 1.38 |
| 12 | 71 | 29 | 17 | 59 | 1.36 |
| 16 | 70 | 30 | 6 | 51 | 1.32 |

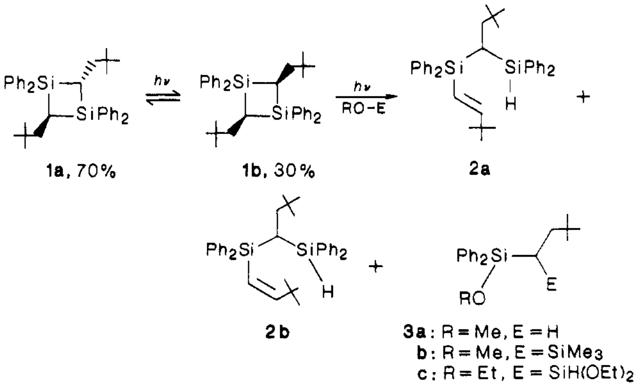
[a] Benzene solvent. Similar results were obtained in cyclohexane solvent. [b] Percent of **1a** and **1b** remaining. [c] Yield of vinylsilanes **2a** and **2b**.

**Table II. Products of the Photolysis of 1 in the Presence of Trapping Agents**

| | % decomp | | product yields[a] | | |
|---|---|---|---|---|---|
| expt | | trapping agent RO–E | 2a | 2b | 3 |
| 1 | 65[b] | none | 27 | 17 | |
| 2 | 97[b] | MeO–H | 35 | 34 | **a**, 20 |
| 3 | 95[c] | MeO–H | 20 | 14 | **a**, 25 |
| 4 | 100[d] | MeO–H | 17 | 12 | **a**, 21 |
| 5 | 76[b] | $MeO–SiMe_3$ | 32 | 18 | **b**, 17 |
| 6 | 95[b] | $EtO–Si(OEt)_2H$ | 32 | 24 | **c**, 20 |

[a] Yields determined using *n*-docosane as an internal standard. [b] Photolysis for 8 h in benzene solvent. Photolysis in cyclohexane gave similar results. [c] Photolysis for 8 h in toluene solvent. [d] Photolysis for 8 h in xylene solvent.

**Scheme I. Photochemical Behavior of 1a and 1b in the Presence of Trapping Agents**



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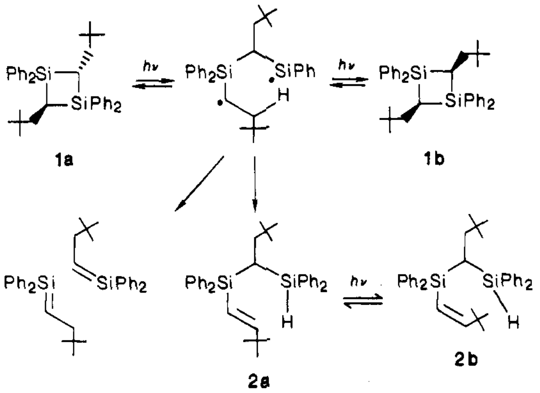
**1a** and **1b** with concomitant formation of the ring-opened isomers **2a** and **2b**. The structural assignment of **2a** and **2b** is based on the coupling constants for the vinyl protons in their $^1$H NMR spectra of 18.9 and 15.8 Hz for the trans and cis isomer, respectively. As has been observed in other systems,[15] the VPC retention time for the trans isomer is shorter than that for the cis. The formation of **2a** and **2b** is consistent with the intermediacy of a 1,4-biradical intermediate produced by photolytic ring opening of the 1,3-disilacyclobutanes. Similar intermediates have been suggested to explain the vinylsilanes observed in the thermolysis of substituted silacyclobutanes.[11]

In contrast to the results reported by Jutzi,[10] the photolysis of either a benzene or a cyclohexane solution of a mixture of **1a** and **1b** in the presence of methanol for 8 h gave three main products, the trans and cis vinylsilane ring-opened isomers of the starting material, **2a** and **2b**, and compound **3a**, (Scheme I and Table II). The formation of **2a** and **2b** is consistent with the formation of a biradical intermediate which undergoes intramolecular hydrogen abstraction more rapidly than it reacts with methanol. The systems for which interception of the biradical intermediate by methanol has been observed do not have hydrogens atom $\beta$ to silicon.[9,10] The presence of such hydrogens in our system permit a convenient six-membered transition state for intramolecular hydrogen transfer to silicon in the 1,4-biradical (Scheme II). Consideration of the steric requirements for this six-membered transition state suggests that an intramolecular hydrogen transfer should result in production of the *trans*-vinylsilane/**2a**. However, after photolyses for 8 h nearly equal amounts of **2a** and **2b** are formed. In one experiment the composition of the product mixture was monitored during the course of the photolysis. At early stages in the photolysis only **2a** is observed. As the photolysis proceeds, the cis isomer **2b** begins to be formed, suggesting that it might not be formed directly from the 1,4-biradical intermediate, but is a photoisomerization product of **2a**. Such photoisomerizations of vinylsilanes have been reported by Seyferth.[16] To test this possibility pure trans isomer **2a** was photolyzed and gave approximately a 50/50 mixture of **2a** and **2b**. Extended photolysis of the vinylsilanes led to the formation of polymeric materials.

Compound **3a** is the expected product from the reaction of methanol with 1,1-diphenyl-2-neopentylsilene. Alkoxysilanes are known to be regiospecific[17] and stereospecific[18] silene traps. When the photolysis of **1** was carried out in the presence of methoxytrimethylsilane, the expected trapped silene product **3b** was obtained in yields comparable to those when methanol was the trap. In both of these trapping experiments isomerization of **1a** to the equilibrium mixture of **1a** and **1b** occurred. This result shows that the isomerization is not due to formation and redimerization of the silene but is better explained by rapid inversion at the carbon radical center and ring closure of the 1,4-biradical intermediate.

In our photolysis experiments the yields of isolated products accounted for from 70 to 90% of the decomposed starting material. To test whether the unaccounted for products could be polymeric materials arising from the presence of silylene intermediates in the reaction the photolysis was carried out in the presence of triethoxysilane. In addition to the vinylsilanes **2a** and **2b** only the alkoxysilane adduct to the silene **3c**[13] was obtained. No products that could be attributed to silylene insertion in the Si–H bond of the trapping agent were observed.

**Scheme II**



In the photolyses conducted in benzene most of the light should be absorbed by benzene, excitation then being transferred to the cyclodisilane **1**. In cyclohexane **1** is the only chromophore present. The fact that we obtain similar results in both solvents is indicative of the production of the same excited arylsilane either directly (cyclohexane) or indirectly by photosensitization (benzene).[19] In order to test whether some of the products arise from the triplet manifold while others originate from the singlet excited-state photolyses with methanol as the trap were conducted by using toluene and xylene solvents. Because these solvents have higher intersystem crossing efficiencies than benzene,[20] the relative amounts of products arising from the triplet state should increase. The results of these experiments (Table II, experiments 3 and 4) show that the amount of trapped silene **3a** remains essentially constant. However the yields of vinylsilanes **2a** and **2b** decrease as does the overall yield of products. This suggests that the triplet excited state(s) of **1** gives (give) rise to nonvolatile products and that the products of the photolysis derive from singlet excited states.

In an attempt to intercept the 1,4-biradical intermediate the photolysis of a mixture of **1a** and **1b** was conducted in the presence of excess tri-*n*-butyltin hydride to give only the vinylsilanes **2a** and **2b**. No 1,1,3,3-tetraphenyl-2-neopentyl-6,6-dimethyl-1,3-disilaheptane, the expected product from hydrogen abstraction by the biradical, was obtained.

## Conclusions

Our results are consistent with the mechanism outlined in Scheme II. Photolysis of the 1,3-disilacyclobutanes gives rise to a singlet 1,4-biradical intermediate which then undergoes one of three competing reactions: ring closure, intramolecular hydrogen abstraction leading to the vinyl silanes, or fragmentation to silene. The fact that ring closure is apparently the most rapid of these processes provides an explanation for the lack of observation of silene products in Jutzi's tetraphenyldisilacyclobutane photolyses,[10] if fragmentation to form silene is not competitive with ring closure in that system. Our results do not rule out a second photochemical process leading directly to a silene, but it is certainly more economical to suggest that

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the 1,4-biradical is the precursor of all the observed products.

## Experimental Section

Benzene was dried by distillation from calcium hydride. Published procedures were used to prepare **1a** and **1b**.[13] Trapping reagents were obtained from Aldrich Chemical Co. and purified by preparative VPC using a $^1/_4$ in. by 10 ft column packed with 20% SE-30 on 60-80 mesh Chromosorb W. All photochemical reactions were carried out in quartz NMR tubes by using a Rayonet RUL-2537A UV lamp (120 W, 254 nm). Reaction mixtures were analyzed by VPC using a 25-m capillary column coated with SE-30 or a 12-m SE-52,54 capillary column with a Varian 3300 gas chromatograph, flame ionization detection, and a Varian 4290 integrator. Product yields were determined by VPC using *n*-docosane as the internal standard. Products were purified for characterization by column chromatography on 270–400 mesh silica gel-60 with *n*-hexane as the eluent. Infrared spectra were recorded on an Analect FX-6160 FT-IR spectrophotometer. $^1$H and $^{13}$C NMR spectra were obtained on a Bruker AM-200-SY spectrometer in CDCl$_3$ solvent, and chemical shifts are reported in parts per million downfield from the internal standard tetramethylsilane. Mass spectra were obtained by using a Hewlett-Packard 5970 GC/MS.

**Photolysis of 1a and 1b in the Presence of Methanol (Table II, Experiment 2).** A solution of 32 mg (0.059 mmol) of **1** and 138 mg (4.31 mmol) of methanol in 1.25 mL of benzene was irradiated. The progress of the photolysis was monitored by VPC. After 8 h of irradiation 97% of the starting material had been consumed. The solvent and methanol were removed under reduced pressure, and the residue was purified by column chromatography to yield **2a** (35%), **2b** (34%), and **3a** (20%) as colorless viscous liquids and high molecular weight products. Similar photolyses were conducted by using toluene and xylene as solvents. The results are given in Table II, experiments 3 and 4.

*trans*-1,1,3,3-Tetraphenyl-2-neopentyl-6,6-dimethyl-1,3-disilahept-4-ene, (**2a**): $^1$H NMR $\delta$ 0.52 (s, 9 H) and 0.89 (s, 9 H) (*t*-Bu), 1.33 (m, 1 H, CH), 1.75 (m, 2 H, CH$_2$), 4.96 (d, $J$ = 2.9 Hz, 1 H, SiH), 5.73 (d, $J$ = 18.9 Hz, 1 H) and 6.10 (d, $J$ = 18.9 Hz, 1 H) (vinyl–H), 7.24–7.52 (m, 20 H, aryl–H); $^{13}$C NMR $\delta$ 2.62 (Si*C*H), 28.78 and 29.36 (C(*C*H$_3$)$_3$), 32.05 and 35.54 (*C*(CH$_3$)$_3$), 38.38 (*C*H$_2$), 117.68 and 162.38 (=*C*H), 127.45, 127.57, 127.64, 128.32, 128.97, 129.15, 134.85, 135.10, 135.46, 135.73, 135.94, 136.07, 136.11, 136.32 (aryl carbons); IR (neat) 2122 cm$^{-1}$ (SiH); MS $m/z$ (relative intensity): 532 (<1, (M$^+$)), 475 (4, (M − *t*-Bu)$^+$), 265 (83, (Ph$_2$SiCH=CHC(CH$_3$)$_3$)$^+$), 209 (84, (Ph$_2$SiCH=CH$_2$)$^+$), 183 (100, Ph$_2$SiH)$^+$). Anal. Calcd for C$_{36}$H$_{44}$Si$_2$: C, 81.14; H, 8.32. Found: C, 82.01; H, 8.30.

*cis*-1,1,3,3-Tetraphenyl-2-neopentyl-6,6-dimethyl-1,3-disilahept-4-ene (**2b**): $^1$H NMR $\delta$ 0.45 (s, 9 H) and 0.76 (s, 9 H) (*t*-Bu), 1.00 (m, 2 H, CH$_2$), 1.60 (m, 1 H, CH), 4.89 (d, $J$ = 2.4 Hz, 1 H, SiH), 5.66 (d, $J$ = 15.8 Hz, 1 H) and 6.60 (d, $J$ = 15.8 Hz, 1 H) (vinyl–H), 6.96–7.81 (m, 20 H, aryl–H); $^{13}$C NMR $\delta$ 4.45 (Si*C*H), 29.37 and 29.51 (C(*C*H$_3$)$_3$), 31.76 and 36.35 (*C*(CH$_3$)$_3$), 38.00 (*C*H$_2$), 118.56 and 163.46 (=*C*H), 127.33, 127.42, 127.68, 128.86, 129.02, 129.12, 134.37, 135.07, 135.58, 136.06, 136.32, 136.64, 137.14 (aryl carbons); IR (neat) 2119 cm$^{-1}$ (SiH); MS $m/z$ (relative intensity) 532 (<1, (M)$^+$), 475 (21, (M − *t*-Bu)$^+$), 265 (100, (Ph$_2$SiCH=CHC(CH$_3$)$_3$)$^+$), 209 (42, (Ph$_2$SiCH=CH$_2$)$^+$), 183 (43, (Ph$_2$SiH)$^+$). Anal. Calcd for C$_{36}$H$_{44}$Si$_2$: C, 81.14; H, 8.32. Found: C, 81.01; H, 8.31.

1,1-Diphenyl-1-methoxy-4,4-dimethyl-1-silapentane (**3a**): $^1$H NMR $\delta$ 0.86 (s, 9 H, *t*-Bu), 1.06–1.17 (m, 2 H, CH$_2$), 1.23–1.36 (m, 2 H, CH$_2$), 3.53 (s, 3 H, OCH$_3$), 7.35–7.61 (m, 10 H, Ar–H); $^{13}$C NMR $\delta$ 7.74 (Si*C*H$_2$), 28.73 (C(*C*H$_3$)$_3$), 31.13 (*C*(CH$_3$)$_3$), 36.59 (*C*H$_2$), 51.83 (O*C*H$_3$), 127.86, 129.78, 134.67, 134.88 (aryl carbons); MS $m/z$ (relative intensity) 213 (100, (Ph$_2$SiOMe)$^+$), 183 ((Ph$_2$SiH)$^+$). Anal. Calcd for C$_{19}$H$_{26}$SiO: C, 76.45; H, 8.78. Found: C, 75.89, H, 8.94.

**Photolysis of 1a and 1b with Methoxytrimethylsilane (Table II, Experiment 5).** To a solution of 20.1 mg (0.038 mmol) of **1** in 0.30 mL of benzene was added 66 mg (0.63 mmol) of methoxytrimethylsilane. Photolysis for 8 h gave 76% decomposition of **1**. Analysis of the reaction products showed **2a** (32%), **2b** (18%), and 1-methoxy-1,1-diphenyl-2-trimethylsilyl-4,4-dimethyl-1-silapentane (**3b**; 17%) along with higher molecular weight products. The properties of **3b** were identical with those previously reported.[13]

**Photolysis of 1a and 1b with Triethoxysilane (Table II, Experiment 6).** To a solution of 34 mg (0.064 mmol) of **1** in 0.67 mL of benzene was added 140 mg (0.856 mmol) of triethoxysilane. After photolysis for 8 h 95% of **1** had decomposed. Three products, **2a** (32%), **2b** (24%), and 1-ethoxy-1,1-diphenyl-2-(diethoxysilyl)-4,4-dimethyl-1-silapentane (**3c**; 20%), were isolated. Spectroscopic data for **3c**:[13] $^1$H NMR $\delta$ 0.76 (s, 9 H, *t*-Bu), 0.97–1.17 (m, 10 H), 1.65 (d, 2 H, CH$_2$), 3.50–3.85 (two overlapping quartets, 6 H, ethoxy CH$_2$'s), 4.59 (d, 1 H, Si–H), 7.30–7.80 (m, 10 H, aryl–H); MS $m/z$ (relative intensity) 430 (7, (M$^+$)), 429 (7, (M − H)$^+$), 401 (14, (M − Et)$^+$), 353 (32), 267 (40), 227 (87, (Ph$_2$SiOEt)$^+$), 183 (100, (Ph$_2$SiH)$^+$), 199 (22), 145 (19), 123 (31), 105 (32); IR (neat) 2124 cm$^{-1}$ (Si–H).

**Photolysis of 1a and 1b with Tri-*n*-butyltin Hydride.** A solution of 60.5 mg (114 mmol) of **1** and 330 mg (1.13 mmol) of tri-*n*-butyltin hydride in 0.97 mL of benzene was photolyzed for 8 h. **1** (59%) had decomposed to give a mixture of products including **2a** (22%) and **2b** (7%). GC/MS analysis of the reaction mixture showed no evidence for trapped radical products.

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**Registry No.** **1a**, 116429-86-8; **1b**, 116429-87-9; **2a**, 121425-52-3; **2b**, 121425-53-4; **3a**, 121425-54-5; **3b**, 116429-88-0; **3c**, 121440-69-5; MeOH, 67-56-1; MeOSiMe$_3$, 1825-61-2; (EtO)$_3$SiH, 998-30-1.