their generous loan of ruthenium.

Registry No. 1, 139565-54-1; 2, 139565-56-3; 3, 139565-58-5; 4, 139565-57-4; 5, 139565-60-9; 5′, 139565-76-7; 6, 139565-62-1; 7, 91083-16-8; 8, 139565-64-3; 9, 80049-65-6; 10, 139565-66-5; 11, 139565-68-7; 12, 139565-70-1; 14, 139565-72-3; 15, 139565-74-5; 16, 3479-30-9; DAPP, 29949-75-5; $[CpRe(CH_3CN)_3]PF_6$, 80049-61-2; $P(OCH_2CH{=}CH_2)_3$, 102-84-1; $PhP(OC_3H_5)_2$, 833-57-8; $Ph_2P(OC_3H_5)$, 14655-53-9; $ClCH_2CH{=}CH_2$, 107-05-1; $PhP(O)(C_3H_5)(OC_3H_5)$, 14655-46-0.

Supplementary Material Available: Listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (*U*'s) (5 pages); a listing of observed and calculated structure factors (×10) (7 pages). Ordering information is given on any current masthead page.

Photochemical Ring-Opening and Expansion Reaction of 2,4-Dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutane

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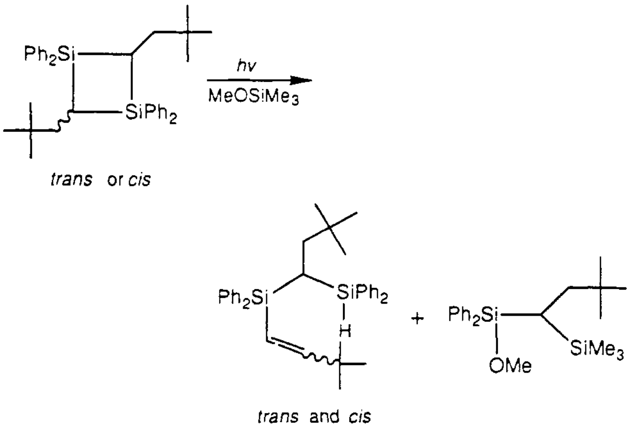
Received August 30, 1991

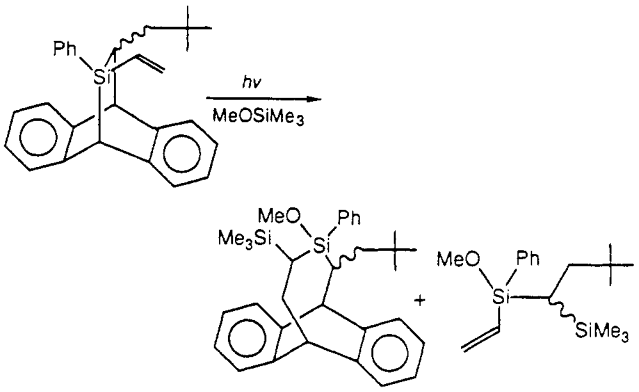
Photolysis of 2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutane (1) in the presence of methanol and methoxytrimethylsilane gives three major products, ring-opened alkenylsilanes, trapping products of silaethenes, and six-membered-ring products. The results are consistent with the initial formation of 1,4-biradical intermediates which undergo three competing reactions: intramolecular hydrogen abstraction leading to alkenylsilanes, fragmentation to silaethenes, and ring closure to six-membered-ring silenes. This is the first evidence for the generation of a six-membered-ring silene by the novel ring-closure reaction involving the vinyl group on silicon.

Introduction

The photochemical behavior of 1,3-disilacyclobutanes has received little attention.[2,3] The first photochemical study of 1,3-disilacyclobutanes was reported by Jutzi.[2] The photolysis of *cis*- or *trans*-2,4-diphenyl-1,1,3,3-tetramethyl-1,3-disilacyclobutane in methanol gave the methanol adduct of 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.[2] In order to look into this conflict, we investigated the photochemical behavior of *trans*- and *cis*-2,4-dineopentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutane.[3] The photolysis of the cyclohexane solution of *trans*- or *cis*-2,4-dineopentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutane in the presence of methoxytrimethylsilane gave *trans*- and *cis*-alkenylsilanes as major products from an intramolecular hydrogen shift reaction in the ring-opened 1,4-biradical intermediate and the trapping adduct of 1,1-diphenyl-2-neopentylsilene as a minor product:



We also recently reported that the photolysis of the silabicyclo[2.2.2]octadiene having a vinyl group on the silicon atom gave the novel cyclic eight-membered-ring silene formed by the ring closure of the 1,6-biradical through vinyl involvement:[4]



In extension of these reactions, we wish to report the results of photochemical reactions of the vinyl-substituted 1,3-disilacyclobutanes 2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutanes (**1a–c**) in the absence and presence of trapping agents such as methanol and methoxytrimethylsilane.

Results and Discussion

The compounds *cis*-2,4-dineopentyl-1,1,3-triphenyl-*trans*-3-vinyl-1,3-disilacyclobutane (**1a**), *trans*-2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutane (**1b**), and *cis*-2,4-dineopentyl-1,1,3-triphenyl-*cis*-3-vinyl-1,3-disilacyclobutane (**1c**) were obtained in yields of 4.2%, 9.2%, and 6.2%, respectively, from the reaction of *tert*-butyllithium with a 1:1 mixture of chlorodivinylphenylsilane and chlorodiphenylvinylsilane in hexane at low temperature.[5]

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(1) (a) Korea Institute of Science and Technology. (b) Yonsei University.

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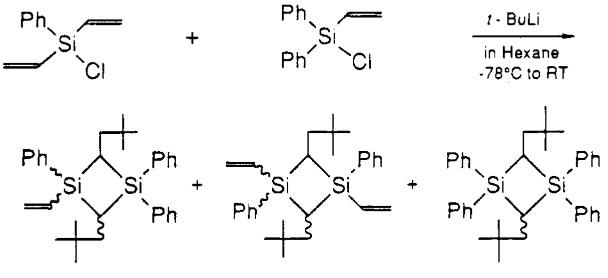
0276-7333/92/2311-1626$03.00/0

Table I. Results of the Photochemical Reaction of 1 in the Absence of Trapping Agent

		reactant, %			product, %					
expt no.	time, h	**1a,b**	**1c**	[a]	**2**[b]	**2a**[d]/**2b**[d]	**3**[c]	**3a**[d]/**3b**[d]	**4a–e**	**5a,b**
1	0	100		100						
	1	56.7	8.5	65.2	13.3	12.3	5.2	12.0	3.4	1.7
	2	27.3	6.7	34.0	26.0	6.4	9.6	4.7	4.1	2.7
	3	11.5	3.1	14.6	27.3	4.5	8.5	4.5	1.7	2.9
	4	4.8	1.4	6.3	28.2	3.2	9.6	4.0	1.5	2.9
2	0	7.3	92.7							
	4	5.9	2.6	8.5	34.8	2.5	8.8	4.5	1.8	2.6

[a] Percent of **1a–c** remaining. [b] Yield of **2a** and **2b**. [c] Yield of **3a** and **3b**. [d] All of the compounds **2a**, **2b**, **3a**, and **3b** were obtained as approximately 50/50 mixtures of two diastereomers, D_1 and D_2.

In addition to **1a–c**, five isomeric 2,4-dineopentyl-1,3-diphenyl-1,3-divinyl-1,3-disilacyclobutanes (**4a–e**;[6] 11.0%) and the two isomers[9] *trans*- (**5a**; 2.3%) and *cis*-2,4-dineopentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutane (**5b**; 2.0%) were also obtained along with polymeric materials:



1a-c, 19.6% 4a-e, 11.0% 5a, b, 4.3%

The photolyses of **1** were carried out in the absence and presence of trapping agents such as methanol and methoxytrimethylsilane. The irradiation of a cyclohexane solution (0.05 M) of **1** for 4 h in the absence of a trapping agent gave the ring-opened alkenylsilanes **2a,b** and **3a,b** and the 1,3-disilacyclobutanes **4a–e** and **5a,b**. The results of the photochemical reaction are summarized in Table I.

The fragmentation patterns of GC/MS spectra for four of the compounds, **2a,b** and **3a,b**, were similar to each other, which strongly suggested that the four compounds were the anticipated isomeric ring-opening products (experiment 1). The structural assignments of **2a,b** and **3a,b** were based on the coupling constants for the alkenyl protons in their ^{1}H NMR spectra of 18.9 and 15.6–15.8 Hz for the trans and cis isomers, respectively, as have been observed in similar systems.[3,8] The diastereomers D_1 and D_2 for each of the compounds **2a,b** and **3a,b** could not be separated under our preparative GC conditions. These diastereomers were partially separated by liquid column chromatography and identified by analyzing NMR spectral data of a diastereomeric mixture containing one particular isomer as a major component. The five isomeric 2,4-dineopentyl-1,3-diphenyl-1,3-divinyl-1,3-disilacyclobutanes (**4a–e**) and two isomeric 2,4-dineopentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutanes (**5a,b**)[9] were identified on the basis of NMR and GC/MS data.

As shown in Scheme I, the formation of compounds **2** and **3** could be explained by the intramolecular hydrogen shift in 1,4-biradical intermediates generated by the photolytic ring opening of 1,3-disilacyclobutanes. Similar intermediates have been suggested to explain the alkenylsilanes observed in the thermolysis of substituted silacyclobutanes.[10] As the photolysis proceeded, amounts of alkenylsilanes **2** and **3** were increased and the ratio of the trans/cis forms of **2** and **3**, respectively, was decreased under our reaction conditions. In Table I, the ratio of trans (**a**) to cis forms (**b**) in **2** and **3** varied from 12.3 and 12.0 after 1 h to 3.2 and 4.5, respectively, after 4 h of irradiation (experiment 1). These results showed that the photolysis of **1** gave trans forms **2a** and **3a** at an early stage and the photoisomerization of **2a** and **3a** to **2b** and **3b**, respectively, occurred later. The consideration of the steric requirements for the six-membered transition state in our system convinced us that an intramolecular hydrogen transfer should result in production of the *trans*-alkenylsilanes **2a** and **3a**, followed by the photochemical isomerization of **2a** and **3a** to **2b** and **3b**, respectively. The formation of **2** (28.2%) was more favorable than that of **3** (9.6%) in the photolysis of **1** (experiment 1). This result seemed to be consistent with the fact that the silaallyl radical intermediate A generated from pathway a was more stable than the silabenzyl radical intermediate B from pathway b (Scheme I). The product yields obtained from the photolysis of **1** (93% **1c**) in experiment 2 were similar to those in experiment 1 with the exception of the increment of **2**. These results might be attributed to the conformational effect of 1,3-disilacyclobutane in the transition state of intramolecular hydrogen abstraction of 1,4-biradical intermediates A and B.

The photoisomerization among **1a–c** occurred to give a mixture containing **1b** as the major component, but a constant ratio of **1a,b** to **1c** was never observed during the photolysis. As shown in Table I, such isomerization might be explained by rapid inversion at the carbon radical center and then ring closure of the 1,4-biradical intermediates A and B or head to tail dimerization of 1,1-diphenyl-2-neopentylsilene with 1-phenyl-1-vinyl-2-neopentylsilene generated from the Si–C bond cleavage of biradical intermediates A and B, although a photochemical process leading directly to silenes is not ruled out.

Five isomeric 2,4-dineopentyl-1,3-diphenyl-1,3-divinyl-1,3-disilacyclobutanes (**4a–e**) and two isomeric 2,4-dineo-

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(5) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013. Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 8447. See also: Auner, N. *J. Organomet. Chem.* **1988**, *353*, 275. Auner, N.; Gleixner, R. *J. Organomet. Chem.* **1990**, *393*, 33.

(6) The individual components of **4a–e** were separated by preparative GLC for spectroscopic studies, and subsequent spectral analyses in comparison with the spectral data of compounds having similar structures[7] led to the assignments of the stereochemistry for the isomers as follows: **4a**, *syn*-(*cis*-2,4-dineopentyl-*cis*-1,3-diphenyl)-1,3-divinyl-1,3-disilabutane, 11.5%; **4b**, *trans*-2,4-dineopentyl-*cis*-1,3-diphenyl-1,3-divinyl-, 20.6%; 4c, *trans*-2,4-dineopentyl-*trans*-1,3-diphenyl-1,3-divinyl-, 27.2%; **4d**, *cis*-2,4-dineopentyl-*trans*-1,3-diphenyl-1,3-divinyl-, 25.1%; **4e**, *anti*-(*cis*-2,4-dineopentyl-*cis*-1,3-diphenyl)-1,3-divinyl-, 15.7%. We are using syn and anti to designate those isomers in which cis-neopentyl and cis-phenyl groups are on the same and opposite sides of the silacyclobutane ring, respectively.

(7) Jones, P. R.; Lee, M. E. *J. Organomet. Chem.* **1982**, *232*, 33.

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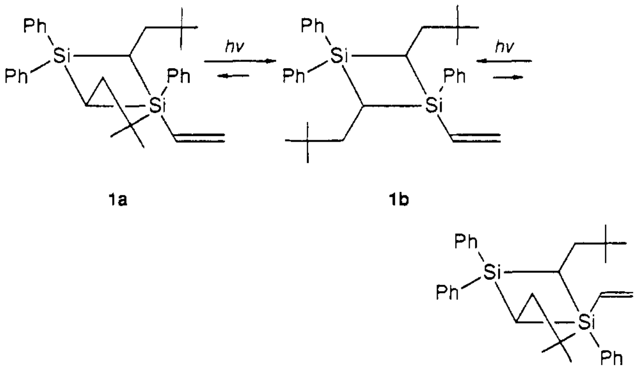
(10) Davidson, I. M. T.; Ostah, N. A.; Seyferth, D.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *187*, 297.



1a

1b

1c

pentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutanes (**5a,b**) were also produced as minor products. The formation of **4** and **5** could be explained by the dimerization of 2-neopentyl-1-phenyl-1-vinylsilene and 1,1-diphenyl-2-neopentylsilene, respectively. The products, **4** and **5**, could undergo further photolysis to give ring-opened alkenylsilane compounds as described in our previous paper.[3]

The photolysis of a cyclohexane solution (0.05 M) of **1** in the presence of methanol gave three major products, alkenylsilanes **2a,b** and **3a,b**, methanol adducts with silaethenes **6** and **7**, and ring-expanded products **8a–d** (Table II and Scheme II).

In contrast to the results reported by Jutzi,[2] methanol adducts with 1,4-biradical intermediates were not observed in our systems. The systems for which the methanol trapping of the biradical intermediate has been observed do not have a hydrogen atom β to silicon.[2,11]

Alkenylsilanes **2a,b** and **3a,b** were obtained in yields comparable to those in the absence of trapping agent. This result strongly indicates that alkenylsilanes **2a,b** and **3a,b** are formed from two biradical intermediates, A and B, which undergo intramolecular hydrogen abstraction more rapidly than methanol addition. The presence of β-hydrogens in our systems permit a convenient six-membered transition state for intramolecular 1,5-hydrogen transfer to silicon in the 1,4-biradical intermediates A and B. Compounds **6** and **7** were the expected products from the trapping reaction of methanol with 2-neopentyl-1-phenyl-1-vinylsilene and 1,1-diphenyl-2-neopentylsilene, respectively.

More significant was the formation of four stereoisomers of six-membered-ring products **8a–d**, obtained in 4.3%, 3.0%, 1.6%, and 0.3% yields, respectively. The stereochemistry of these isomers was established by the analysis of ^{1}H and ^{13}C NMR data. The most likely precursors to **8** are the six-membered cyclic silene intermediates C and D, generated from the radical ring-closure reaction through the vinyl group involvement in the 1,4-biradical intermediate A (Scheme III). The ring-expansion pathway to a six-membered-ring product in the photochemical reaction of silacyclobutane having a vinyl group on the silicon atom has not been observed previously but has considerable precedent in the photochemical reaction of the 3-vinylsilacyclobutane leading to ring-expanded product involving the vinyl group on carbon.[12] By analogy with monosilacyclobutane, it is useful to postulate biradical intermediates in a mechanistic sequence leading to six-membered-ring silene intermediates.

Yields of isomers **8a,b**, produced from the reaction of the six-membered-ring silene intermediate C with methanol, were higher than those of isomers **8c,d** from the intermediate D. These results are consistent with the fact that the formation of six-membered-ring silene C is more favorable than that of D in light of the interaction between two bulky neopentyl groups at the ring. In the methanol addition to six-membered-ring silenes C and D, methanol attack from the bottom is more favorable than attack from the top due to steric hindrance between two neopentyl groups at ring silenes. Therefore, yields of isomers **8a,c** in the trapping reaction of six-membered-ring silenes with methanol are higher than those of isomers **8b,d**, respectively.

In order to test the presence of free silenes C and D, the photolysis was carried out in the presence of methoxytrimethylsilane, which is known to be a regiospecific[13] and stereospecific[14] silene trap. Thus, the irradiation of a cyclohexane solution (0.05 M) of **1** with excess methoxytrimethylsilane for 4 h gave 92% decomposition and produced three isomeric ring-expanded products, **11a–c**, in 6% yield. In addition, also alkenylsilanes **2a,b** and **3a,b** and adducts with silaethene **9** and **10** were obtained in yields similar to those when methanol was the trap (Table II). The formation of **11** can be also explained as described for that of **8**. These results indicated that the free silene intermediates, silaethenes, leading to products **9** and **10**, and the six-membered-ring silenes (C and D), which led to ring-expanded products (**11a–c**), were formed under our photolysis conditions.

In the photolyses of **1** with trapping agents, yields of ring-expanded products obtained from **1a,b** were higher than those from **1c**. However, yields of alkenylsilanes from **1a,b** were less than those from **1c**. These results might be also attributed to the conformational effect of 1,3-disilacyclobutane, as described above in the formation of compounds **2** and **3**.

In an attempt to trap silene intermediates, the photolysis of **1** was conducted in the presence of excess 2,3-dimethylbutadiene to give **2a,b** and **3a,b**. The expected products from the reaction of 2,3-dimethylbutadiene with silenes was not observed.

On the basis of the results, the mechanisms for the photochemical reactions of vinyl-substituted 1,3-disilacyclobutanes can be outlined as shown in Schemes I and III. Photolyses of the 2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutanes give rise to 1,4-biradical intermediates which undergo three competing reactions: intramolecular hydrogen abstraction leading to the alkenylsilanes, fragmentation to silaethenes, and ring closure to six-membered-ring silenes. Although photochemical processes leading directly to silaethene and six-membered-ring silenes (C and D) are not ruled out, it seems more reasonable to suggest that the 1,4-biradical intermediates A and B are precursors of all the observed products. This is the first evidence for the generation of a six-membered-ring silene by a novel ring-closure reaction involving the vinyl group on silicon.

Experimental Section

Cyclohexane was dried by distillation from sodium benzophenone ketyl prior to use. Methoxytrimethylsilane was obtained from Petrarch Systems. All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. All

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[11] Valkovich, P. B.; Ito, T. I.; Weber, W. P. *J. Org. Chem.* **1974**, *39*, 3543.

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[14] Jones, P. R.; Bates, T. F.; Cavley, A. H.; Arif, A. M. *J. Am. Chem. Soc.* **1986**, *108*, 3122. Yoo, B. R.; Jung, I. N.; Lee, M. E.; Kim, C. H. *Bull. Korean Chem. Soc.* **1991**, *12*, 517.

Scheme I

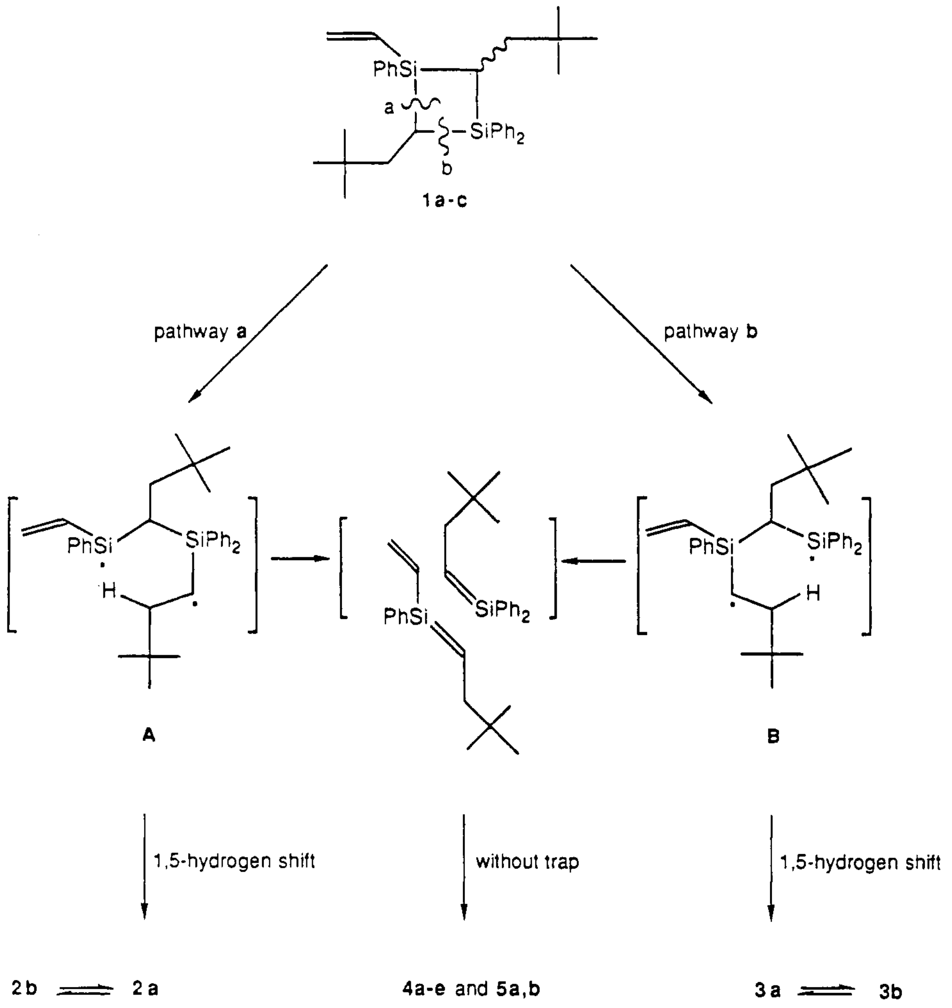


Table II. Products of the Photolysis of 1[a] in the Presence of Trapping Agents

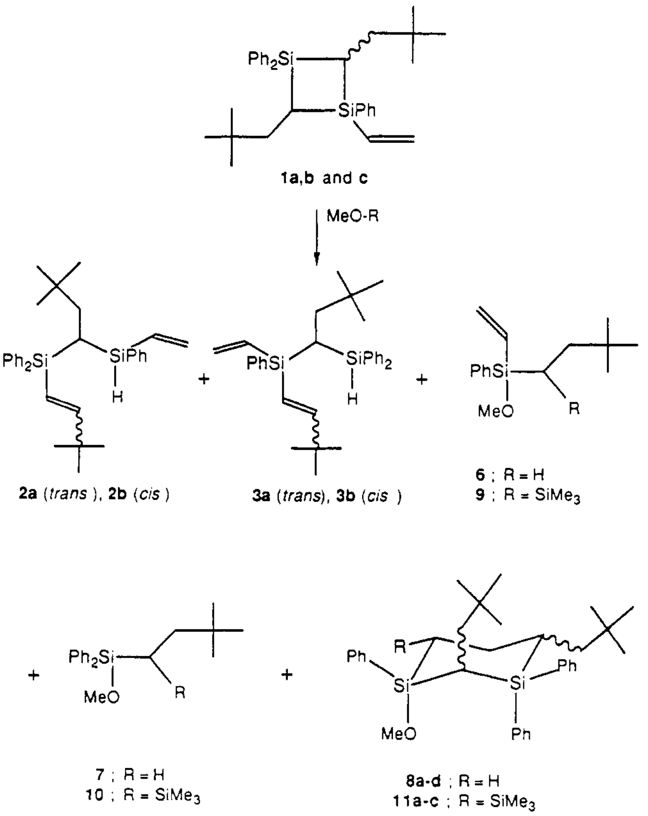
	reactant		product yield,[b] %					
			alkenylsilane					
expt no.	% decompn	trapping agent RO–E	**2**[c]	**2a/2b**	**3**[d]	**3a/3b**	silaethene adduct	ring-expanded product (**a**:**b**:**c**:**d**)
1	93.8	none	28.2	3.2	9.6	4.0		
3	90.6	Me–OH	24.2	3.2	8.2	3.1	**6**, 14.3; **7**, 17.3	**8**, 9.2 (4.3:3.0:1.6:0.3)
4	91.8	MeO–SiMe$_3$	22.4	2.2	6.5	2.7	**9**,[e] 14.7; **10**, 15.1	**11**, 6.0 (3.7:0.6:1.7:–)

[a] A mixture of **1a** (30%) and **1b** (70%). [b] Yields determined using *n*-docosane as an internal standard. [c] Yield of **2a** and **2b**. [d] Yield of **3a** and **3b**. [e] Ratio of the two diastereomers D$_1$:D$_2$ was 55:45.

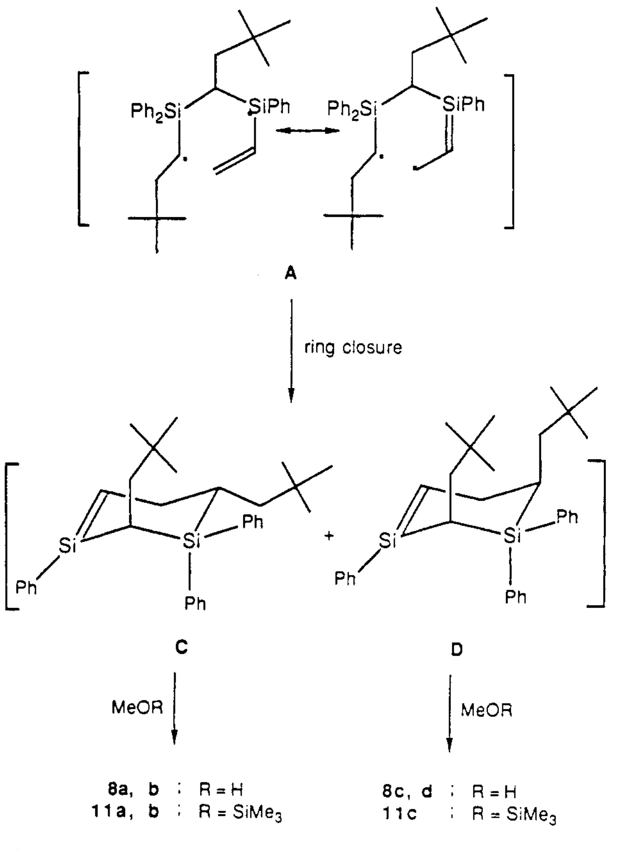
air-sensitive liquids and the dried solvents were transferred by standard syringe or double-tipped-needle techniques. All photochemical reactions were carried out in 5-mm quartz NMR tubes using a Rayonet RUL-2537A UV lamp (120 W, 254 nm). Reaction mixtures were analyzed by GLC over a 12-m capillary column coated with SE-52 or 54 using a Varian 3300 gas chromatograph, with a flame ionization detector and a Varian 4290 integrator. Product yields were determined by GLC using *n*-docosane as the internal standard. Samples for characterization were purified by column chromatography on 27–400 mesh silica gel 60G with a *n*-hexane–methylene chloride mixture as the eluent or collected on a Varian Aerograph series 1400 gas chromatograph (with thermal conductivity detector) with a 4.5-m by $^1/_8$-in. stainless steel column packed with 15% SE-30 on 60–80 mesh Chromosorb W. Samples for photochemical reaction were collected on a Spectra-Physics Iso Chrom LC pump with Spectra 100 variable-wavelength detector and 250 mm × 22.5 mm Alltech HPLC column packed with Econosphere silica gel 10 μm. Proton, carbon, and 2D (proton–proton correlation) NMR spectra were obtained on a Bruker AM 500 or a Varian Gem 300 spectrometer in chloroform-*d*; chemical shifts are reported in parts per million downfield from the tetramethylsilane internal standard. Mass spectra were obtained using a Hewlett-Packard 5970 or 5987X GC/MS instrument. Elemental analyses were performed by the Chemical Analysis Laboratory of the Korea Institute of Science and Technology. High-resolution (HR) mass spectra were obtained at the Korea Basic Science Center on a VG 70-SEQ mass spectrometer at an ionizing voltage of 70 eV. High-resolution mass spectra of the two isomers **a** and **b** were obtained as representatives among four and three isomers in **8a–d** and **11a–c**, respectively.

Reaction of *tert*-Butyllithium with a Mixture of Chlorodivinylphenylsilane and Chlorodiphenylvinylsilane. To a stirred solution of 3.45 g (17.8 mmol) of chlorodivinylphenylsilane and 4.35 g (17.8 mmol) of chlorodiphenylvinylsilane in 150 mL of dry *n*-hexane cooled to −78 °C by using a dry ice–acetone bath was added dropwise 10.5 mL of *tert*-butyllithium (Aldrich) diluted to 1.7 M in pentane. The white precipitate which formed dissolved when the reaction solution was washed with 70 mL of a saturated aqueous ammonium chloride solution. The organic layer was separated, combined with three hexane extractions of the aqueous layer, and dried with anhydrous magnesium sulfate. After evaporation of the solvent using a rotary evaporator, 8.0 g of a viscous yellow oil was obtained, which GLC analysis indicated

Scheme II. Products of the Photolysis of 1 in the Presence of Trapping Agents



Scheme III



to be 19.6% of **1a–c**, 11.0% of **4a–e**, and 4.3% of **5a,b**. The dimers were separated from the products by a liquid chromatographic column. The column, 2.5 cm × 80 cm, was packed with 70–230 mesh normal-phase silica gel. The eluent was hexane. Separation of dimers by liquid chromatography indicated that the first eluted dimers were **4a–e** and the last eluted dimers were **5a,b**. The components of **1a–c** for photochemical reactions were separated by HPLC and also characterized by NMR analysis.

1a: ^{1}H NMR δ 0.74 (s, 18 H, $C(CH_3)_3$), 1.24–1.77 (m, 6 H, CH and CH_2), 6.00 (dd, $J = 4.1, 20.0$ Hz, 1 H), 6.24 (dd, $J = 4.1, 14.7$ Hz, 1 H) and 6.62 (dd, $J = 14.7, 20.0$ Hz, 1 H) (vinyl H), 7.23–7.67 (m, 15 H, aryl H); ^{13}C NMR δ 8.56 (*C*H), 29.28 ($C(CH_3)_3$), 31.82 ($C(CH_3)_3$), 39.74 (CH_2), 127.32, 127.37, 127.53, 127.61, 127.72, 127.77, 127.80, 129.17, 129.17, 129.25, 129.34, 134.24, 134.97, 135.23, 135.32, 135.39, 135.44, 135.47, 135.60, 136.30, 136.87 (overlapping carbons of aryl and vinyl groups of **1a,b**).

1b: ^{1}H NMR δ 0.61 and 0.73 (s, 9 H, $C(CH_3)_3$), 1.24–1.77 (m, 6 H, CH and CH_2), 6.06 (dd, $J = 4.0, 19.8$ Hz, 1 H), 6.32 (dd, $J = 4.0, 14.7$ Hz, 1 H), and 6.48 (dd, $J = 14.7, 19.8$ Hz, 1 H) (vinyl H), 7.23–7.67 (m, 15 H, aryl H); ^{13}C NMR δ 10.05 and 13.78 (*C*H), 29.15 and 29.28 ($C(CH_3)_3$), 31.79 and 32.82 ($C(CH_3)_3$), 38.89 and 39.74 (CH_2), other (aryl and vinyl carbons of **1b** were overlapped with those of **1a** as mentioned above).

1c: ^{1}H NMR δ 0.72 (s, 18 H, $C(CH_3)_3$), 1.27 (t, $J = 6.6$ Hz, 2 H, CH), 1.69 (d, $J = 6.6$ Hz, 4 H, CH_2), 5.96 (dd, $J = 4.2, 20.0$ Hz, 1 H), 6.38 (dd, $J = 4.2, 15.0$ Hz, 1 H) and 6.52 (dd, $J = 15.0, 20.0$ Hz, 1 H) (vinyl H), 7.39–7.72 (m, 15 H, aryl H); ^{13}C NMR δ 13.42 (*C*H), 28.32 ($C(CH_3)_3$), 31.73 ($C(CH_3)_3$), 40.11 (CH_2), 127.50, 127.74, 127.85, 127.93, 129.15, 129.23, 129.31, 132.64, 134.16, 134.35, 134.97, 135.60, 136.70, 137.46 (aryl and vinyl carbons).

The mass spectra for all three isomers **1a–c** were very similar: m/z (relative intensity) 482 (6, M^+), 426 (6), 425 (37, $(M - t\text{-Bu})^+$), 371 (14), 341 (10), 327 (11), 301 (10), 266 (6), 265 (27), 259 (26), 216 (7), 215 (33), 210 (15), 209 (73), 184 (16), 183 (100, $(Ph_2SiH)^+$), 181 (24), 159 (35), 133 (31), 131 (17), 121 (13), 107 (34), 105 (40), 57 (33). Anal. Calcd for $Si_2C_{32}H_{42}$: C, 79.60; H, 8.77. Found for a mixture of dimers, **1a–c**: C, 79.14; H, 8.89.

4a: ^{1}H NMR δ 0.76 (s, 18 H, $C(CH_3)_3$), 1.08 (t, $J = 6.3$ Hz, 4 H, CH_2), 1.60 (d, $J = 6.3$ Hz, 4 H, CH_2), 5.93 (dd, $J = 4.1, 20.1$ Hz, 2 H), 6.19 (dd, $J = 4.1, 14.5$ Hz, 2 H), and 6.54 (dd, $J = 14.5, 20.1$ Hz, 2 H) (vinyl H), 7.32–7.64 (m, 10 H, aryl H); ^{13}C NMR δ 10.24 (*C*H), 29.48 ($C(CH_3)_3$), 31.89 ($C(CH_3)_3$), 40.03 (CH_2), 126.57, 127.05, 128.65, 133.07, 135.66, 139.19 (aryl and vinyl carbons).

4b: ^{1}H NMR δ 0.57 and 0.79 (s, 9 H, ($C(CH_3)_3$), 1.19 (m, 2 H, CH), 1.55 (m, 4 H, CH_2), 6.00 (dd, $J = 4.0, 19.8$ Hz, 2 H), 6.31 (dd, $J = 4.0, 14.6$ Hz, 2 H) and 6.46 (dd, $J = 14.6, 19.8$ Hz, 2 H) (vinyl H), 7.30–7.70 (m, 10 H, aryl H); ^{13}C NMR δ 8.19 and 12.98 (*C*H), 29.25 and 29.48 ($C(CH_3)_3$), 31.89 and 31.93 ($C(CH_3)_3$), 38.64 and 39.65 (CH_2), 127.49, 127.95, 129.40, 135.28, 135.01, 136.38 (aryl and vinyl carbons).

4c: ^{1}H NMR δ 0.76 (s, 18 H, $C(CH_3)_3$), 1.32 (t, 2 H, CH), 1.57 (d, 4 H, CH_2), 6.05 (dd, $J = 4.2, 19.5$ Hz, 2 H), 6.36 (dd, $J = 4.2, 14.6$ Hz, 2 H), and 6.42 (dd, $J = 14.6, 19.5$ Hz), 7.30–7.70 (m, 10 H, aryl H); ^{13}C NMR δ 8.82 (*C*H), 29.24 ($C(CH_3)_3$), 31.77 ($C(CH_3)_3$), 39.80 (CH_2), 127.8, 129.3, 134.8, 135.2, 135.6, 135.9 (aryl and vinyl carbons).

4d: ^{1}H NMR δ 0.72 (s, 18 H, $C(CH_3)_3$), 1.09 (t, $J = 6.8$ Hz, 2 H, CH), 1.56 (d, $J = 6.8$ Hz, 4 H, CH_2), 5.89 (dd, $J = 3.6, 20.2$ Hz, 1 H), 5.99 (dd, $J = 3.4, 20.2$ Hz, 1 H), 6.23 (dd, $J = 3.6, 14.6$ Hz, 1 H), 6.34 (dd, $J = 3.4, 14.3$ Hz, 1 H), 6.52 (dd, $J = 14.3, 20.2$ Hz, 1 H), 6.52 (dd, $J = 14.4, 20.2$ Hz) and 6.60 (dd, $J = 14.6, 20.2$ Hz, 1 H) (vinyl H), 7.31–7.67 (m, 10 H, aryl H); ^{13}C NMR δ 12.17 (*C*H), 29.73 ($C(CH_3)_3$), 31.77 ($C(CH_3)_3$), 39.26 (CH_2), 127.53, 127.84, 129.18, 132.82, 133.02, 133.32, 133.96, 135.30, 135.94, 137.29, 138.19 (aryl and vinyl carbons).

4e: ^{1}H NMR δ 0.72 (s, 18 H, $C(CH_3)_3$), 1.09 (t, $J = 6.5$ Hz, 2 H, CH), 1.69 (d, $J = 6.5$ Hz, 4 H, CH_2), 5.97 (dd, $J = 5.4, 20.1$ Hz, 2 H), 6.36 (dd, $J = 5.4, 15.0$ Hz, 2 H) and 6.49 (dd, $J = 15.0, 20.1$ Hz, 2 H) (vinyl H), 7.37–7.67 (aryl H); ^{13}C NMR δ 13.15 (*C*H), 29.32 ($C(CH_3)_3$), 31.21 ($C(CH_3)_3$, 40.15 (CH_2), 127.81, 128.77, 133.20, 134.13, 136.06, 139.34 (aryl and vinyl carbons).

The mass spectra for all five isomers **4a–e** were very similar: m/z (relative intensity) 432 (2, M^+), 375 (25, $(M - t\text{-Bu})^+$), 291 (14), 277 (15), 215 (46), 209 (56), 183 (59), 159 (100), 133 (75), 131 (45), 105 (57), 57 (83). Anal. Calcd for $Si_2C_{28}H_{40}$: C, 77.71; H, 9.32. Found for a mixture of dimers, **4a–e**: C, 77.41; H, 9.48.

Photolysis of 1a,b in the Absence of a Trapping Agent (Experiment 1). A solution of a mixture of **1a** (30%) and **1b** (70%) (17.8 mg, 0.037 mmol) in 0.74 mL of cyclohexane was irradiated. The progress of the photolysis was monitored by GLC. After 4 h of irradiation 93.8% of the starting material was decomposed. The solvent was removed under reduced pressure, and a residue was obtained which GLC analysis indicated to be alkenylsilanes **2a** (21.5%), **2b** (6.7%), **3a** (7.7%), and **3b** (1.9%) and 1,3-disilacyclobutanes **4a–e** (1.5%) and **5a,b** (2.9%). The reaction mixture collected from several repeated experiments was purified by column chromatography as described above. Thus, **2a-D$_1$** was separated as a pure liquid but other isomers were obtained as a mixture containing one particular isomer as a major component and characterized by the analyses of spectral data. The properties of **5**[9] were identical with those previously reported.

***trans*-5,5-Diphenyl-6-(phenylvinylsilyl)-2,2,8,8-tetramethyl-5-silanon-3-ene (2a-D$_1$)**: ^{1}H NMR δ 0.68 and 0.97 (s, 9 H, $C(CH_3)_3$), 0.85 (ddd, J = 2.5, 2.6, 7.0 Hz, 1 H, CH), 1.72 (dd, J = 2.5, 14.0 Hz, 1 H) and 1.80 (dd, J = 7.0, 14.0 Hz, 1 H) (CH_2), 4.61 (dd, J = 2.6, 5.1 Hz, 1 H, SiH), 5.82 and 6.15 (d, J = 18.9 Hz, 1 H) (alkenyl H), 5.80 (dd, J = 4.3, 19.7 Hz, 1 H), 6.14 (dd, J = 4.3, 14.6 Hz, 1 H), and 6.30 (ddd, J = 5.1, 14.6, 19.7 Hz, 1 H) (vinyl H), 7.22–7.57 (m, 15 H, aryl H); ^{13}C NMR δ 2.75 (SiCH), 28.85 and 29.36 ($C(CH_3)_3$), 32.06 and 35.47 ($C(CH_3)_3$), 38.75 (CH_2), 117.40 and 162.15 (alkenyl carbons), 127.45, 127.60, 127.67, 127.68, 128.95, 129.02, 134.29, 134.47, 134.95, 135.65, 136.03, 136.15 (aryl and vinyl carbons).

2a-D$_2$: ^{1}H NMR δ 0.63 and 0.97 (s, 9 H, $C(CH_3)_3$), 0.75–1.13 (m, 1 H, CH), 1.68–1.85 (m, 2 H, CH_2), 4.64 (dd, J = 1.5, 4.5, Hz, 1 H, SiH), 5.86 and 6.17 (d, J = 18.9 Hz, 1 H) (alkenyl H), 5.76 (dd, J = 4.3, 19.5 Hz, 1 H), 5.99 (dd, J = 4.3, 14.4 Hz, 1 H) and 6.14 (ddd, J = 4.5, 14.4, 19.5 Hz, 1 H) (vinyl H), 7.25–7.57 (m, 15 H, aryl H); ^{13}C NMR δ 3.30 (CH), 28.86 and 29.38 ($C(CH_3)_3$), 32.22 and 35.61 ($C(CH_3)_3$), 39.23 (CH_2), 117.81 and 162.39 (alkenyl carbons), 127.47, 128.88, 129.03, 129.17, 134.50, 135.12, 135.16, 135.44, 135.57, 135.77, 135.83, 136.12 (aryl and vinyl carbons).

***cis*-5,5-Diphenyl-6-(phenylvinylsilyl)-2,2,8,8-tetramethyl-5-silanon-3-ene (2b-D$_1$ (2b-D$_2$))**: ^{1}H NMR δ 0.6 (0.59) and 0.78 (0.78) (s, 9 H, $C(CH_3)_3$), 0.7–1.15 (m, 2 H, CH), 1.53–1.75 (m, 4 H, CH_2), 4.54 (br dd, J = 1.8, 4.9 Hz, 2 H, Si–H), 5.66 and 6.63 (d, J = 15.7 Hz, 2 H) (alkenyl H), 5.39–6.2 (m, 6 H, vinyl H), 7.15–7.87 (m, 30 H, aryl H). ^{13}C NMR δ 5.24 (5.68) (CH), 29.35 (29.31) and 29.54 (29.54) ($C(CH_3)_3$), 31.87 (31.85) and 36.17 (36.38) ($C(CH_3)_3$), 38.63 (38.85) (CH_2), 118.60 (118.61) and 163.41 (163.24) (alkenyl carbons), 127.45–137.2 (22 peaks, aryl and vinyl carbons).

The mass spectra for isomers **2a,b** were very similar: m/z (relative intensity) 482 (9, M^+), 426 (26), 425 (61, $(M - t\text{-Bu})^+$), 398 (19), 372 (11), 371 (30), 347 (28), 341 (21), 322 (12), 266 (11), 265 (41), 209 (10), 184 (18), 183 (100), 181 (31), 159 (45), 145 (16), 135 (23), 133 (57), 132 (14), 131 (29), 121 (36), 109 (12), 108 (10), 107 (82), 105 (16), 103 (95), 73 (14), 59 (32), 57 (96), 55 (25).

***trans*-5-Phenyl-5-vinyl-6-(diphenylsilyl)-2,2,8,8-tetramethyl-5-silanon-3-ene (3a-D$_1$ (3a-D$_2$))**: ^{1}H NMR δ 0.61 (0.62) and 0.90 (0.95) (s, 9 H, $C(CH_3)_3$), 0.70–1.15 (m, 2 H, CH), 1.67–1.85 (m, 4 H, CH_2), 4.98 (br dd, J = 1.3, 2.7 Hz, 2 H, Si–H), 5.55 (5.55) and 6.07 (6.11) (d, J = 18.9 Hz, 1 H) (alkenyl H), 5.63–6.39 (m, 6 H, vinyl H), 7.24–7.72 (m, 30 H, aryl H).

***cis*-5-Phenyl-5-vinyl-6-(diphenylsilyl)-2,2,8,8-tetramethyl-5-silanon-3-ene (3b-D$_1$ (3b-D$_2$))**: ^{1}H NMR δ 0.55 (0.52) and 0.91 (0.87) (s, 9 H, $C(CH_3)_3$), 0.7–1.15 (m, 2 H, CH), 1.53–1.75 (m, 4 H, CH_2), 5.01 (br d, 2 H, Si–H), 5.50 (5.48) and 6.56 (6.53) (d, J = 15.9 Hz, 1 H) (alkenyl H), 5.67–6.47 (m, 6 H, vinyl H), 7.15–7.87 (m, 30 H, aryl H).

The mass spectra for isomers **3a,b** were very similar: m/z (relative intensity) 482 (9, M^+), 426 (24), 425 (58, $(M - t\text{-Bu})^+$), 398 (17), 371 (18), 348 (11), 347 (27), 342 (12), 341 (30), 322 (17), 315 (11), 265 (11), 215 (27), 207 (35), 184 (12), 183 (62), 181 (28), 159 (14), 145 (13), 135 (14), 133 (51), 132 (12), 131 (32), 121 (35), 101 (11), 107 (62), 106 (14), 105 (73), 83 (12), 73 (18), 69 (14), 59 (26), 57 (100). Anal. Calcd for $Si_2C_{32}H_{42}$: C, 79.60; H, 8.77. Found for a mixture of **2** and **3**: C, 79.39; H, 8.79.

Photolysis of 1 (93% 1c) in the Absence of a Trapping Agent (Experiment 2). This experiment was carried out in the same manner as above, with the exception that a mixture of **1a** (2.2%), **1b** (5.1%), and **1c** (92.7%) (22.0 mg, 0.047 mmol) was photolyzed. The reaction products were obtained in yields similar to those in experiment 1 with the exception of the increment of **2** (**2a**, 24.9%; **2b**, 9.9%).

Photolysis of 1a,b in the Presence of Methanol (Experiment 3). A solution of a mixture of **1a** (30%) and **1b** (70%) (17.0 mg, 0.035 mmol) and 90 mg (2.8 mmol) of methanol in 0.71 mL of cyclohexane was irradiated. After 4 h of irradiation 90.6% of the starting material had been consumed. Analysis of the reaction product showed alkenylsilanes **2a** (18.5%), **2b** (5.7%), **3a** (6.2%), and **3b** (2.0%), methanol adducts with silaethenes **6** (14.3%) and **7** (17.3%), and ring-expanded products **8a–d** (9.2%). The ring-expanded products were purified by preparative gas chromatography, and subsequent spectral analyses led to the assignments of the stereochemistry for the isomers as of 2,4-dineopentyl-1-methoxy-1,3,3-triphenyl-1,3-disilacyclohexane as follows: **8a** 1*RS*,2*SR*,4*RS*, 4.3%; **8b**, 1*SR*,2*SR*,4*RS*, 3.0%; **8c** (1*RS*,2*SR*,4*RS*, 1.6%; **8d** 1*SR*,2*SR*,4*RS*, 0.3%.

8a: ^{1}H NMR δ 0.62 and 0.77 (s, 9 H, $C(CH_3)_3$), 0.80 (br d, J = 7.8 Hz, 1 H) and 1.10 (dd, J = 8.8, 13.8 Hz, 1 H) (CH_2), 1.18 (ddd, J = 3.1, 8.8, 11.8 Hz, 1 H) (CH), 1.38–1.43 (m, 2 H), 1.49–1.58 (m, 2 H), 1.68 (dd, J = 7.8, 14.2 Hz, 1 H) (CH_2), 1.70 (td, J = 3.4, 11.8 Hz, 1 H) and 2.25 (tdd, J = 3.1, 3.4, 13.8 Hz, 1 H) (ring CH_2), 3.45 (s, 3 H, OCH_3), 7.13–7.70 (m, 15 H, aryl H); ^{13}C NMR δ 9.64 (CH_2), 14.27 (CH), 23.90 (CH_2), 27.61 (CH), 29.27 and 29.82 ($C(CH_3)_3$), 31.43 and 32.47 ($C(CH_3)_3$), 38.94 and 44.22 (CH_2–$C(CH_3)_3$), 50.50 (OCH_3), 127.19, 127.27, 127.37, 127.47, 127.66, 128.77, 128.92, 129.01, 129.25, 129.42, 134.06, 135.11, 135.85, 136.19, 136.80, 137.12 (aryl carbons were overlapped with those of **8c**); HRMS m/e calcd for $Si_2C_{33}H_{46}O$ 514.3075, found 514.3091.

8b: ^{1}H NMR δ 0.35 and 0.86 (s, 9 H, $C(CH_3)_3$), 0.89 (dd, J = 4.4, 5.0 Hz, 1 H) (CH_2), 1.06–1.15 (m, 2 H) (CH and CH_2), 1.24 (dd, J = 9.1, 14.1 Hz, 1 H), 1.41 (ddd, 4.1, 9.1, 13.2 Hz, 1 H), 1.40–1.59 (m, 3 H), 1.82 (tdd, J = 4.1, 10.9, 15.2 Hz) and 2.25 (dddd, J = 3.2, 4.1, 7.6, 13.6 Hz, 1 H) (ring CH_2), 3.32 (s, 3 H, OCH_3), 7.20–7.76 (m, 15 H, aryl H); ^{13}C NMR δ 4.54 (CH_2), 11.28 (CH), 21.02 (CH_2), 26.06 (CH), 28.82 and 30.20 ($C(CH_3)_3$), 31.63 and 32.64 ($C(CH_3)_3$), 35.75 and 43.50 ($CH_2C(CH_3)_3$), 50.43 (OCH_3), 127.75, 128.82, 128.90, 129.34, 134.88, 135.30, 135.43, 135.48, 135.87, 136.53, 136.69, 136.84 (aryl carbons); HRMS m/e calcd for $Si_2C_{33}H_{46}O$ 514.3075, found 514.3097.

8c: ^{1}H NMR δ 0.39 and 0.82 (s, 9 H, $C(CH_3)_3$), 1.01 (dd, J = 9.0, 14.2 Hz, 1 H) (CH_2), 1.12 (ddd, J = 6.5, 11.4, 15.5 Hz, 1 H) and 1.22 (td, J = 5.0, 15.5, Hz, 1 H) (CH_2), 1.39–1.49 (m, 3 H), 1.69 (dd, J = 4.1, 14.2 Hz, 1 H), 1.82 (tdd, J = 5.0, 11.4, 11.5 Hz, 1 H) and 2.10–2.18 (br m, 1 H) (ring CH_2), 3.53 (s, 3 H, OCH_3), 7.24–7.67 (m, 15 H, aryl H); ^{13}C NMR δ 4.84 (CH_2), 11.25 (CH), 21.01 (CH_2), 26.19 (CH), 29.11 and 29.99 ($C(CH_3)_3$), 31.40 and 32.51 ($C(CH_3)_3$), 36.25 and 43.81 (CH_2–$C(CH_3)_3$), 50.60 (OCH_3), aryl carbons were overlapped with those of **8a** as mentioned above.

8d: ^{1}H NMR δ 0.13 and 0.80 (s, 9 H, $C(CH_3)_3$), 0.34 (dd, J = 2.8, 4.4 Hz), 3.57 (s, 3 H, OCH_3), other protons were overlapped with those of **8c** as mentioned above; ^{13}C NMR δ 11.66 (CH_2), 13.94 (CH), 20.84 (CH_2), 25.69 (CH), 28.90 and 29.53 ($C(CH_3)_3$), 30.93 and 32.48 ($C(CH_3)_3$), 35.93 and 42.16 (CH_2), 51.10 (OCH_3), aryl carbons were overlapped with those of **3b** as mentioned above.

Photolysis of 1 (93% 1c) in the Presence of Methanol. This experiment was carried out in the same manner as experiment 3, except that a mixture of **1a** (2.2%), **1b** (5.1%), and **1c** (92.7%) (27.0 mg, 0.050 mmol) was irradiated. Yields of products were as follows: **2a**, 23.8%; **2b**, 8.9%; **3a**, 6.7%; **3b**, 1.7%; **6**, 16.0%; **7**, 17.7%; **8a–d**, 3.7%.

Photolysis of 1a,b in the Presence of Methoxytrimethylsilane (Experiment 4). This experiment was carried out in the same manner as experiment 3, except that methoxytrimethylsilane was used as trapping agent. Yields of reaction products were as follows: **2a**, 15.4%; **2b**, 7.0%; **3a**, 4.8%; **3b**, 1.7%; **4**, 14.7%; **9**, 14.7%; **10**, 15.1%; **11a**, 3.7%; **11b**, 0.6%; **11c**, 1.7%; **11d**, trace. The properties of **9**[4] (two diastereomers, D$_1$ and D$_2$) and **10**[9] were identical with those previously reported.

(1*RS*,2*SR*,4*RS*,6*RS*)-2,4-Dineopentyl-1-methoxy-6-(trimethylsilyl)-1,3,3-triphenyl-1,3-disilacyclohexane (11a): ^{1}H NMR δ −0.17 (s, 9 H, $Si(CH_3)_3$), 0.37 and 0.79 (s, 9 H, $C(CH_3)_3$), 0.46 (t, J = 7.3 Hz, 1 H) (CH), 0.85 (dd, J = 3.4, 9.8 Hz, 1 H) and 0.98 (dd, J = 8.8, 14.3 Hz, 1 H) (CH_2), 1.48–1.55 (m, 3 H, CH and CH_2), 1.73–1.78 (br m, 1 H, CH), 1.90 (ddd, J = 7.2, 10.0, 14.0 Hz, 1 H) and 2.25 (ddd, J = 4.0, 7.6, 14.0 Hz, 1 H) (ring CH_2), 3.61 (s, 3 H, OCH_3), 7.14–7.71 (m, 15 H, aryl H); ^{13}C NMR δ −0.17 (s, 9 H, $Si(CH_3)_3$), 6.63 (CH), 13.74 (CH), 20.28 (CH_2), 27.75 (CH), 29.51 and 30.22 ($C(CH_3)_3$), 31.70 and 32.29 ($C(CH_3)_3$), 37.76 and 43.83 (CH_2), 51.38 (OCH_3), 127.39, 128.88, 129.00, 129.49, 134.32, 134.55, 134.87, 135.83, 135.93, 136.01, 136.80, 137.07 (aryl carbons); HRMS m/e calcd for $Si_3C_{36}H_{54}O$ 586.3468, found 586.3497.

(1*SR*,2*SR*,4*RS*,6*SR*)-2,4-Dineopentyl-1-methoxy-6-(trimethylsilyl)-1,3,3-triphenyl-1,3-disilacyclohexane (11b): ^{1}H NMR δ −0.08 (s, 9 H, $Si(CH_3)_3$), 0.70 and 0.76 (s, 9 H, $C(CH_3)_3$), 2.44 (ddd, J = 2.2, 7.6, 9.8 Hz), 3.62 (s, 3 H, OCH_3), 7.14–7.70 (m, 15 H, aryl H), other protons were overlapped with those of **11c** as mentioned below; ^{13}C NMR δ 0.26 (s, $Si(\mathit{C}H_3)_3$), 6.69 ($\mathit{C}H$), 14.13 ($\mathit{C}H$), 15.45 ($\mathit{C}H_2$), 22.66 ($\mathit{C}H$), 29.34 and 29.79 ($C(\mathit{C}H_3)_3$), 31.48 and 32.45 ($\mathit{C}(CH_3)_3$), 36.74 and 44.89 ($\mathit{C}H_2C(CH_3)_3$), 51.67 ($O\mathit{C}H_3$), aryl carbons were overlapped with those of **11c** as mentioned below.

(1*RS*,2*SR*,4*SR*,6*SR*)-2,4-Dineopentyl-1-methoxy-6-(trimethylsilyl)-1,3,3-triphenyl-1,3-disilacyclohexane (11c): ^{1}H NMR δ 0.02 (s, 9 H, $Si(CH_3)_3$), 0.63 and 0.74 (s, 9 H, $Si(CH_3)_3$), 0.89 (dd, J = 2.7, 16.4 Hz, 1 H) (CH), 0.96–1.03 (m, 1 H) and 1.12 (t, J = 4.5 Hz, 1 H) (CH_2), 1.19–1.35 (m, 2 H) (CH), 1.51 (dd, J = 8.3, 13.3 Hz, 1 H), 1.64 (dd, J = 4.5, 13.8 Hz, 1 H) (CH_2), 1.75 (t, J = 13.0 Hz, 1 H) (CH_2), 2.04 (ddd, J = 2.7, 5.1, 14.1 Hz, 1 H) (ring CH_2), 3.41 (s, 3 H, OCH_3), 7.14–7.70 (m, 15 H, aryl H); ^{13}C NMR δ 0.09 ($Si(\mathit{C}H_3)_3$), 4.58 ($\mathit{C}H$), 9.90 ($\mathit{C}H$), 15.92 ($\mathit{C}H_2$), 21.84 ($\mathit{C}H$), 29.39 and 30.00 ($C(\mathit{C}H_3)_3$), 31.60 and 32.45 ($\mathit{C}(CH_3)_3$), 37.82 and 44.89 ($\mathit{C}H_2C(CH_3)_3$), 51.20 ($O\mathit{C}H_3$), 127.16, 127.27, 127.39, 127.68, 127.90, 128.83, 129.07, 129.23, 129.50, 134.33, 134.91, 134.99, 135.08, 135.24, 135.83, 135.95, 136.04, 136.10, 136.40, 136.78, 137.07 (aryl carbons were overlapped with those of **11b**); HRMS *m/e* calcd for $Si_3C_{36}H_{54}O$ 586.3468, found 586.3459.

Photolysis of 1 (93% 1c) in the Presence of Methoxytrimethylsilane. This experiment was carried out in the same manner as experiment 4, except that a mixture of **1a** (2.2%), **1b** (5.1%), and **1c** (92.7%) (28.4 mg, 0.059 mmol) was irradiated. Yields of products were as follows: **2a**, 20.0%; **2b**, 11.1%; **3a**, 5.6%; **3b**, 2.1%; **9**, 18.0%; **10**, 15.5%; **11a–c**, 2.7%. The ratio of the two diastereomers D_1:D_2 in **9** was 40:60.

Photolysis of 1a,b in the Presence of 1,3-Dimethylbutadiene. A solution of a mixture of **1a** (30%) and **1b** (70%) (13.0 mg, 0.027 mmol) in 0.54 mL of cyclohexane was photolyzed for 4 h. 1 (83.0%) had decomposed to give a mixture of products including **2a** (20.0%), **2b** (4.7%), **3a** (6.9%), and **3b** (trace). GC/MS analysis of the reaction mixture was not observed for trapped silene products.

Acknowledgment. This research was supported financially by the Ministry of Science and Technology.

Uranium–Ligand Bond Dissociation Enthalpies in Uranium(IV) Polypyrazolylborate Complexes

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Received August 28, 1991

Reaction-solution calorimetry measurements of the enthalpies of alcoholysis of a series of complexes of the type $[HB(3,5\text{-}Me_2Pz)_3]UCl_2L$, where Pz = pyrazolyl and L = O-*t*-Bu, $OCH(CMe_3)_2$, $N(SiMe_3)_2$, $CH(SiMe_3)_2$, and C_5H_5 led to the following uranium–ligand bond dissociation enthalpies, D(U–L), kJ/mol: 460.5 ± 5.0 (O-*t*-Bu), 334 ± 10 ($N(SiMe_3)_2$), 295 ± 11 ($CH(SiMe_3)_2$), 362 ± 12 (C_5H_5). These results, which are anchored on D(U–Cl) = 422.6 kJ/mol, were compared with early literature data for other uranium systems. Together with extended Hückel molecular orbital calculations, they provided some ground to address the discrepancy between the uranium–ligand bond dissociation enthalpies obtained from iodinolysis and alcoholysis reactions.

Introduction

There has been a considerable interest in the thermochemistry of uranium organometallic compounds. Most of the available data have recently been reported by three groups. Marks and co-workers made reaction-solution calorimetry studies involving the complexes $U(Cp')_3L$ (L = Me, Bu, CH_2SiMe_3, CH_2Ph, $CHCH_2$, CCPh, CO, I),[1] $U(C_5H_4Me)_3thf$,[1] $U(Cp^*)_2L_2$ (L = Me, CH_2Ph, CH_2SiMe_3),[2] $U(Cp^*)_2(Cl)L$ (L = Me, Ph, CH_2Ph),[2] and $U(Cp^*)_2[OSi(t\text{-}Bu)Me_2]L$ (L = H, Me),[2] where $Cp' = \eta^5\text{-}Me_3SiC_5H_4$ and $Cp^* = \eta^5\text{-}C_5Me_5$. Bettonville, Goffart, and Fuger have also used reaction-solution calorimetry to examine the complexes $U(C_9H_7)_3L$ (L = Me, I)[3,4] and $U(1\text{-}EtC_9H_6)_3Me$,[3] where C_9H_7 = indenyl. Finally, the enthalpies of formation of the compounds $U(Cp)_3L$ (L = $i\text{-}C_4H_9$, OC_4H_9, Cp, Cl)[5,6] and $U(C_8H_8)_2$,[5] where Cp = $\eta^5\text{-}C_5H_5$, have been determined by Telnoy and co-workers, by using static-bomb combustion calorimetry. A very large discrepancy between Telnoy's value for $\Delta H_f°[U(C_8H_8)_2,cr]$, 326.4 ± 12.6 kJ/mol, and the one obtained by Kuznetsov et al.,[7] 131 ± 15 kJ/mol, by using the same technique, suggests that static-bomb combustion calorimetry is probably not the best option to study these systems (see also discussion below). Kuznetsov et al. have also reported the enthalpy of formation of $U(C_8H_7Bu)_2$ and derived uranium–butylcyclooctatetraene mean bond dissociation enthalpy.[8] A gas-

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