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Photochemical reactions of [5,6 : 7,8]dibenzo-2-silabicyclo[2.2.2]octanes

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Abstract

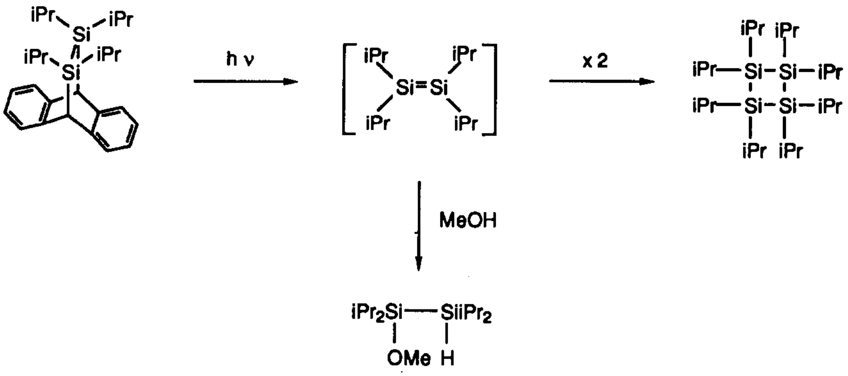
The photochemical reactions of 2-*R*-2-phenyl[5,6 : 7,8]dibenzo-2-silabicyclo[2.2.2]octanes (R = Ph, **1**, R = Me, **5**) in cyclohexane have been studied in the presence or absence of trapping agents such as methanol and methoxytrimethylsilane. The photolysis of **1** in the presence of methanol gave 9-(1,1-diphenylmethoxysilyl-3,3-dimethylbutyl)-9,10-dihydroanthracene as the major product and the methanol adduct of 1,1-diphenyl-2-neopentylsilene as the minor product. When trimethylmethyoxysilane was used as the trap, the silene adduct was only isolated in small quantity and no 9,10-disubstituted anthracene product was obtained.

The photolysis of pure *Z*-**5** or *E*-**5** in the absence of trapping agent gave *Z*–*E* photoisomerization products and polymeric products. During the photolysis a constant ratio of *Z*-**5** and *E*-**5** was never observed because the formation of high molecular weight products was faster than isomerization. The major product of photolysis of pure *E*-**5** or *Z*-**5** in the presence of methanol or deuterated methanol was *SS*(*RR*), **6**, and *RS*(*SR*), **6′**, respectively, at early stages of the reaction but the other diastereomer was produced also as the photolysis proceeded. Photoisomerization of the diastereomers **6** and **6′** also occurred. The 1,6-biradical intermediates formed from *Z*- and *E*-**5** retain their asymmetry at the silicon atom prior to the abstraction of methoxy group from methanol, but not at carbon.

Introduction

The photolysis and pyrolysis of [5,6 : 7,8]dibenzo-2-silabicyclo[2.2.2]octanes have received considerable attention in the last few years, principally because the systems generate reactive intermediates such as silenes [1] or disilenes [2] via retro-Diels–Alder reactions. Jones and Lee investigated the thermolysis of 2-methyl-2-phenyl-3-neopentyl[5,6 : 7,8]dibenzo-2-silabicyclo[2.2.2]octane [1]. They observed the formation of a silene intermediate which was trapped stereospecifically with trimethylmethoxysilane, thus indicating that the configuration of the silene is stable up to 300 ° C.

In 1984 Nagai and coworkers reported that tetraisopropyldisilene was obtained from the photolysis of 2,2,3,3-tetraisopropyl[5,6 : 7,8]dibenzo-2,3-disilabicyclo-[2.2.2]octane [2]. The disilene was trapped with methanol to give 1,1,2,2-tetraisopro-



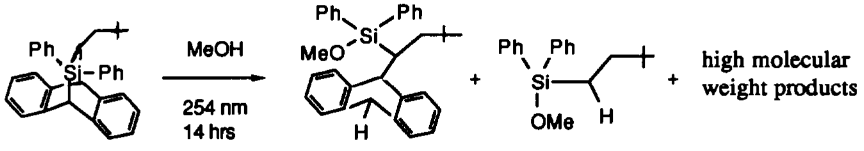
Scheme 1.

pylmethoxydisilane, and dimerized to octaisopropylcyclotetrasilane in the absence of trapping agents (Scheme 1). In both of these cases, [4 + 2]-cycloreversion was claimed. It is well known that [4 + 2]-cycloreversion proceeds thermally, but not photochemically, with retention of configuration [3]. This prompted us to investigate the photochemical behaviour of 2-*R*-2-phenyl-3-neopentyl[5,6 : 7,8]dibenzo-2-silabicyclo[2.2.2]octanes, **1** and **5**.

Results and discussion

Compound **1**, 2,2-diphenyl-3-neopentyl[5,6 : 7,8]dibenzo-2-silabicyclo[2.2.2]octane, was prepared by a previously reported method [4].

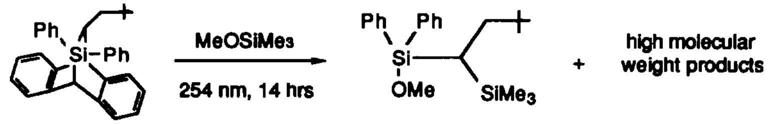
The photolysis of a 0.06 *M* solution of **1** in cyclohexane in the presence of methanol for 14 h gave two products, 9-(1-diphenylmethoxysilyl-3,3-dimethylbutyl)-9,10-dihydroanthracene, **2** (57%), and 4,4-dimethyl-1,1-diphenyl-1-methoxy-1-silapentane, **3** (16%), as shown in eq. 1. Overall decomposition was 92% based on 8% recovery of unreacted **1**. The major product, **2**, was produced by the trapping reaction of methanol with the 1,6-biradical intermediate formed by the cleavage of the benzylic C–Si bond. The interception of biradical intermediates by methanol has been reported by Weber [5] and Jutzi [6].



(eq.1)

1, 92% decomp. 2, 57% 3, 16%

The expected product, **3**, was obtained as the minor product. To test if **3** was produced from the reaction of methanol with 1,1-diphenyl-2-neopentylsilene, methoxytrimethylsilane (known [7] to be a regiospecific and efficient silene trap) was used as a trapping agent. When a 0.06 *M* cyclohexane solution of **1** was irradiated for 14 h in the presence of methoxytrimethylsilane, 45% of the starting material was consumed giving 4,4-dimethyl-1,1-diphenyl-1-methoxy-2-trimethylsilyl-1-silapentane, **4** (17%), and high molecular weight products (eq. 2). **4** was obtained in a yield comparable to that of **3** when methanol was the trap. It is noteworthy that the product 2 was not obtained, indicating that methoxytrimethylsilane does not serve as a biradical trapping agent. This result demonstrates that the free silene intermediate, 1,1-diphenyl-2-neopentylsilene, was generated under our photolysis conditions.



(eq. 2)

1, 45% decomp.

4, 17%

In order to investigate the stereochemistry of the photochemical reaction, *Z*- and *E*-2-methyl-2-phenyl-3-neopentyl[5,6 : 7,8]dibenzo-2-silabicyclo[2.2.2]octanes, **5**, were prepared by a standard method [1,8]. The photolysis of *Z*- and *E*-**5** was carried out in the presence or absence of trapping agents such as methanol and deuterated methanol. The photolysis of a 0.06 *M* solution of pure *Z*-**5** or *E*-**5** in cyclohexane gave *Z*–*E* photoisomerization products and high molecular weight products. The percentages of *Z*-**5** or *E*-**5** obtained from the photolysis of pure *Z*-**5** and *E*-**5** in the absence of trapping agents are compared in Figs. 1 and 2.

After 12.5 h of irradiation 71% of pure *Z*-**5** was isomerized to *E*-**5** (24%) and other high molecular weight products appeared, and the percentages of both isomers decreased slowly as photolysis proceeded, in step with an increase of the ratio of *E*-**5**/*Z*-**5**. Photolysis for 45 h gave 96% decomposition of **5** and a 1/3 mixture of *Z*-**5**/*E*-**5**. At no time during photolysis was a constant ratio of *Z*-**5** or *E*-**5** observed. This indicates that the formation of high molecular weight products was faster than the isomerization of *Z*-**5** to *E*-**5**.

On the other hand, 26.5% of *E*-**5** was decomposed and 2% of *Z*-**5** was produced after 12 h of irradiation. The ratio of *E*-**5**/*Z*-**5** decreased as the photolysis pro-

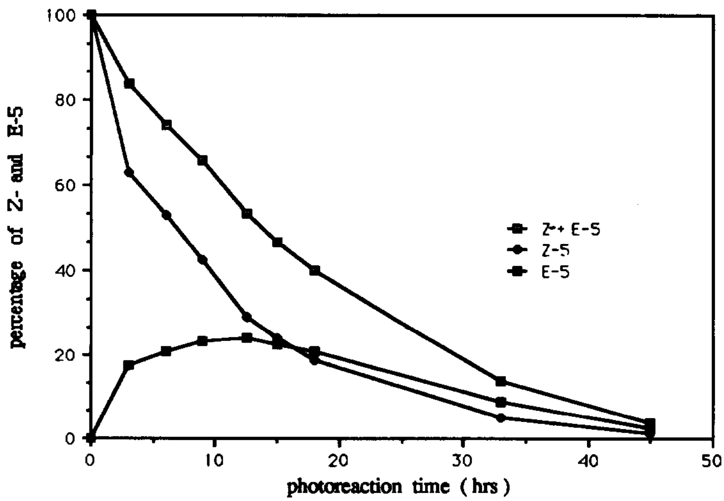


Fig. 1. Percentage distribution of *Z*- and *E*-**5** in the photolysis of *Z*-**5**.

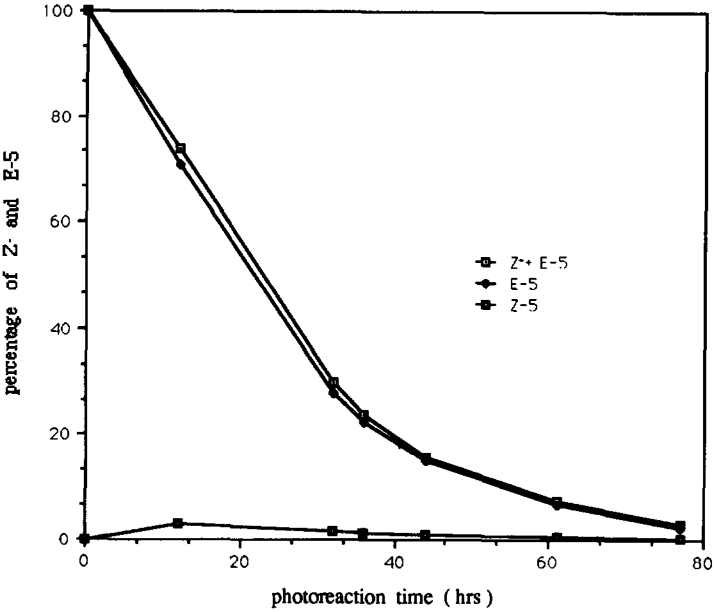


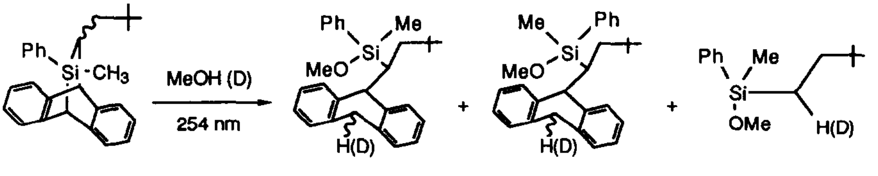
Fig. 2. Percentage distribution of *Z*- and *E*-**5** in the photolysis of *E*-**5**.

ceeded (Fig. 2). After 68 h of irradiation 95% of *E*-**5** was decomposed to give 0.4% of *Z*-**5** along with high molecular weight products.

Comparison of Fig. 1 and Fig. 2 is instructive. Of the starting materials, *Z*-**5** is faster than *E*-**5** to decompose and to isomerize. This is explicable in terms of relief of repulsion due to *cis–vicinal* interaction of the phenyl group and neopentyl group in the six-membered ring.

The photolysis of a 0.06 *M* cyclohexane solution of *Z*-**5** and *E*-**5** in the presence of methanol gave two diastereomers, 9-(1-methylphenylmethoxysilyl-3,3-dimethylbutyl)-9,10-dihydroanthracenes, **6**, **6′** as the major and 2-methoxy-2-phenyl-5,5-dimethyl-2-silahexane, **7**, as shown in eq. 3.

Yields of products obtained from the photolysis of *Z*-**5** and *E*-**5** in the presence of methanol are summarized in Table 1. In the case of *Z*-**5**, after 2 h of irradiation decomposition of *Z*-**5** occurred to the extent of 73% to give two diastereomers of the methanol-trapped anthracene products, **6** (0.9%) and **6′** (49.1%), and the methanol-trapped silene adduct, **7** (8%). The recovered starting material consisted of *Z*-**5** (26.0%) and *E*-**5** (1.2%) (expt. 1). The 0.9 to 49.1 ratio of **6** to **6′** might represent about 98% retention of stereochemistry at silicon. This indicates that the silyl radicals formed were retaining asymmetry prior to the abstraction of methoxy group from methanol, as has been proposed for another process which may also involve a



(eq. 3)

Z-5 and E-5   SS (RR) - 6   RS (SR) - 6′   7

Table 1

Products of the photolysis of *Z*-**5** and *E*-**5** in the presence of methanol

Expt.	Reaction time (h)	Reaction mixture				
		Z-**5** and *E*-**5** remaining (%)		Product yields [a] (%)		
		Z-**5**	*E*-**5**	**6**	**6′**	**7**
1	0	99.0	1.0			
	2	26.0	1.2	0.9	49.1	8.0
	6	1.7	0.9	8.5	60.0	9.0
2	0	2.1	97.9			
	2	1.7	74.3	9.7	1.3	2.6
	6	0.6	43.9	28.3	5.9	8.0
	12	trace	9.4	39.9	13.0	8.0

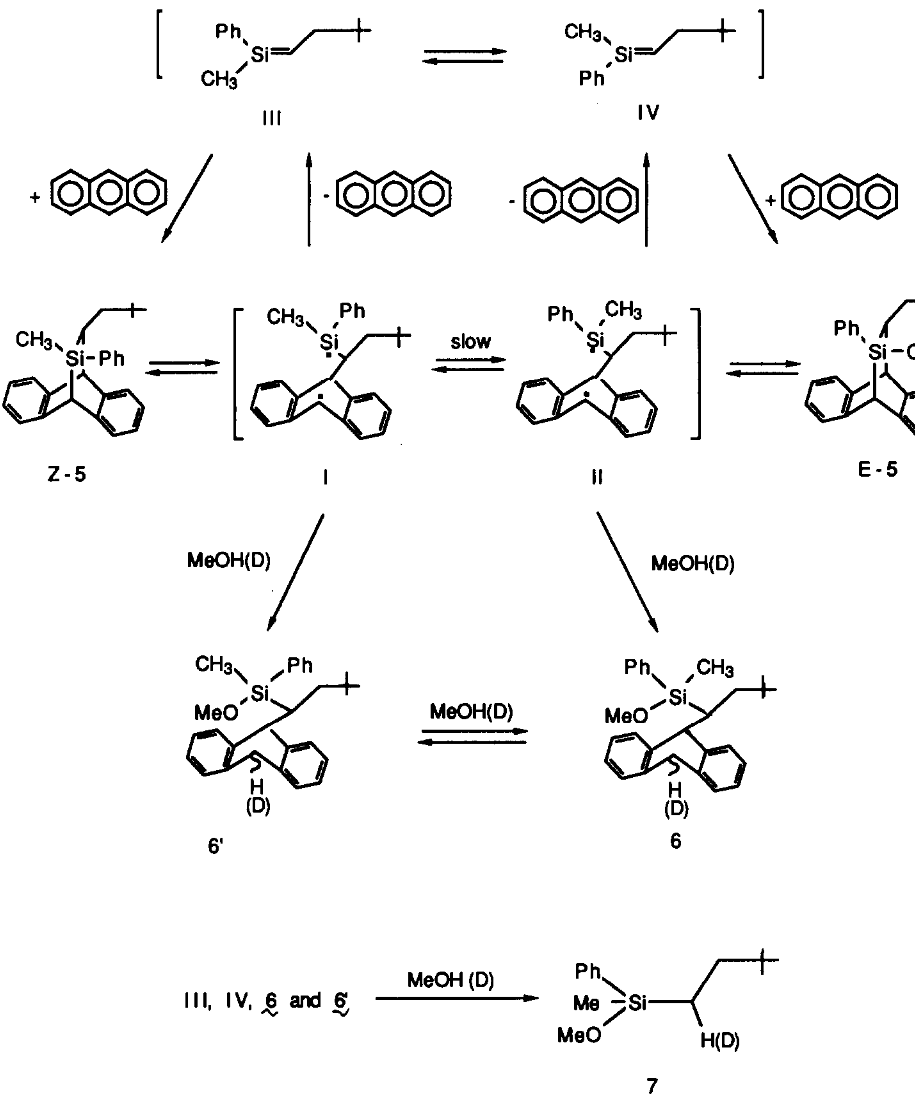
[a] Yields were determined using n-docosane as an internal standard.

chiral radical [9]. After 6 h of irradiation 97% of the starting material was decomposed. Two diastereomers, **6** (8.5%) and **6′** (60.0%), and a silene adduct, **7** (9%) were produced. The recoveries of starting material were 1.7% of *Z*-**5** and 0.9% of *E*-**5**. The 8.5 to 60 ratio of **6** to **6′** represents about 88% retention of stereochemistry at silicon. The formation of two diastereomers, **6** and **6′**, as the major products, is consistent with the formation of a 1,6-biradical intermediate via the cleavage of the benzylic C–Si bond. The possible pathways for the photolysis of *Z*- and *E*-**5** with methanol are summarized in Scheme 2. In contrast to the result obtained from the photolysis of *Z*-**5** in the absence of trapping agents, the photolysis of *Z*-**5** in the presence of methanol showed that the stereoretention of the starting material was very high at an early stage. The ratio of **6** to **6′** increased as the photolysis proceeded. The results show that trapping of the 1,6-biradical intermediate generated from *Z*-**5** by methanol or ring closure is faster than inversion of the silicon radical [9].

To obtain mechanistic information on potential intermediates, deuterium-labelling studies of the photolyses of *Z*-**5** and *E*-**5** were carried out using methanol-O-d_1 as the trapping agent, and yields were similar to those obtained when methanol was the trapping agent. Deuterium atoms were found at *syn* (minor) and *anti* (major) positions on 10-carbon which is consistent with a free radical reaction in **6** and **6′**, and was also found at the α-carbon of **7**.

In the case of *E*-**5**, after 2 h of irradiation 24% of the starting material was decomposed to give two diastereomers, **6** (9.7%) and **6′** (1.3%), and **7** (2.6%). The starting materials were recovered at the rates: 1.7% *Z*-**5** and 74.3% *E*-**5**, as shown in Table 1 (expt. 2). After 6 h of irradiation 55.5% of the starting material was consumed. The yield of two diastereomers was 28.3% of **6** and 5.9% of **6′**, and 8.0% of the methanol-trapped silene product, **7** was obtained. Recovery of starting material was 0.6% of *Z*-**5** and 43.9% of *E*-**5**. After 12 h of irradiation 90.6% of *E*-**5** was decomposed to give **6** (39.9%), **6′** (13.0%) and **7** (8.0%). Of the starting materials a trace of *Z*-**5** was recovered and 9.4% of *E*-**5**.

In the presence of methanol isomerization of *Z*-**5** to *E*-**5** occurred. These results are explained by inversion at the silicon radical center of **I** and ring closure of the



Scheme 2. Photochemical behavior of *Z*-5 and *E*-5 in the presence of methanol.

1,6-biradical intermediate, II, or isomerization of *Z*-silene, III, to *E*-silene, IV, as has been proposed for the isomerization of disilene [10] and the reaction of *E*-silene with anthracene, although a secondary photochemical process leading directly to a silene is not ruled out. In both cases, the methanol-trapped anthracene products showed marked retention of stereochemistry at silicon at an early stage but this decreased as photolysis proceeded.

To test for isomerization of methanol-trapped anthracene products, **6** and **6′** were photolyzed individually in the presence of methanol. The percentage distributions in the photoisomerization of **6** and **6′** are summarized in Table 2. In the case of the photolysis of **6**, after 2 h of irradiation GC analysis showed 80.2% of **6** and 3.5% of **6′** along with 1.4% of **7**, and then the percentages of **6** and **6′** varied from

Table 2

Percentage distribution in the photoisomerization of **6** and **6′** in the presence of methanol

Expt.	Reaction time (h)	Compound		
		6	**6′**	**7**
3	0	99.0	1.0	
	2	80.2	3.5	1.4
	6	53.8	16.6	2
	12	32.4	21.6	1.0
4	0	1.2	98.8	
	6	12.3	60.1	2
	12	24.1	32.7	1.4

53.8 and 16.6 after 6 h to 32.4 and 21.6 after 12 h of irradiation (expt. 3). This result indicates that the photolysis of *Z*-**5** with methanol gave **6** and **7** at an early stage and the photoisomerization of **6** to **6′** began as photolysis proceeded. Extended photolysis of **6** and **6′** led to the formation of products of high molecular weight. In the case of the photolysis of **6′**, the reaction products were identical with those of photolysis of **6** with methanol. The percentages of the diastereomers **6** and **6′** were 12.3 and 60.1 after 6 h, and 24.1 and 32.7 after 12 h of irradiation (expt. 4). This shows that the photolysis of *E*-**5** with methanol gave **6′** and **7** at an early stage and the photoisomerization of **6′** to **6** began as the photolysis proceeded. The photoisomerization rate of **6′** to **6** was similar to that of **6** to **6′**.

Experimental

Cyclohexane was dried by distillation from sodium ketyl benzophenone prior to use, and methanol-O-*d* was obtained from Aldrich Chemical Company. Methoxytrimethylsilane was obtained from Petrarch Systems. All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. All 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-52,54 using a Varian 3300 gas chromatograph, flame ionization detector, and a Varian 4290 integrator. Product yields were determined by GLC using n-docosane as the internal standard. Diastereomer analysis of the methanol-trapped anthracene products, **6** and **6′**, was accomplished by programming from 180 to 220 °C at 1 °C/min. Samples for characterization were purified by column chromatography on 270–400 mesh silica gel 60G dried for 4 h at 150 °C with an n-hexane–CH_2Cl_2 mixture as the eluent. A Varian aerograph series 1400 gas chromatograph (with thermal conductivity detector) was used with a 4.5 m by 1/8 inch stainless steel column packed with 15% SE-30 on 60–80 mesh chromosorb W. Proton, carbon and 2D (proton–carbon correlation) NMR spectra were obtained on Bruker AM 200-SY and AC 300P spectrometers in CCl_4 or $CDCl_3$; chemical shifts are reported in parts per million down-field from the tetramethylsilane internal standard. Mass spectra were obtained using a Hewlett Packard 5970 GC/MS. Elemental analyses were performed by the Chemical Analysis Laboratory of the Korea Institute of Science and Technology.

*Photolysis of **1** with methanol*

A solution of 28.7 mg (0.065 mmol) of **1** and 51 mg (1.55 mmol) of methanol in 1.1 ml of cyclohexane was irradiated. The photolysis was monitored by GLC. After 14 h of irradiation 92% of the starting material had been consumed. The solvent and methanol were removed under reduced pressure, and the residue was purifed by column chromatography to yield **2** (57%), and **3** (16%) as a yellow viscous liquid and as high molecular weight products.

For **2**: ^{1}H-NMR: 0.50 [s, 9H, $C(CH_3)$], 1.72–1.93 (m, 3H, CH and CH_2, 3.23 (s, 3H, OCH_3), [3.63 (d, 1H, J 18.3 Hz), 4.12 (d, 1H, J 18.3 Hz) and 4.39 (d, 1H, J 7.2 Hz) (benzyl-H)], 6.90–7.41 (m, 18H, aryl-H). ^{13}C-NMR: 28.49 (CH), 29.53 [$C(CH_3)_3$], 31.87 [$C(CH_3)_3$], 38.74 (CH_2), 36.17 and 48.04 (benzyl-carbons), 51.29 (OCH_3), 125.35, 125.48, 125.64, 126.07, 127.24, 127.40, 127.67, 127.73, 128.89, 129.11, 129.43, 134.51, 134.93, 135.14, 135.33, 137.81, 138.13, 139.31, 141.14 (aryl-carbons). MS m/z (relative intensity): 213 [15, $(Ph_2SiOMe)^+$], 183 [10, $(Ph_2SiH)^+$], 180 (21), 179 (100, $C_{14}H_{11}{}^+$) *, 178 (35), 105 (5), 59 (4), 57 (3). Anal. Found: C, 83.48; H, 7.47. Calc. for $C_{33}H_{36}SiO$: C, 83.14; H, 7.61%.

*Photolysis of **1** with methoxytrimethylsilane*

To a solution of 27.0 mg (0.061 mmol) of **1** in 1 ml of cyclohexane was added 77 mg (0.74 mmol) of methoxytrimethylsilane. Photolysis for 14 h gave 45% decomposition of **1**. Analysis of the reaction products showed **4** (17%) along with higher molecular weight products. The product of **4** were identical with those previously reported [4].

*Photolysis of Z-**5** with methanol (expt. 1)*

A solution of 22.9 mg (0.06 mmol) of *Z*-**5** and 70 mg (2.12 mmol) of methanol in 1 ml of cyclohexane was irradiated. After 6 h of irradiation 97% of *Z*-**5** had decomposed. The reaction mixture showed three products, **6** (8.5%), **6′** (60.0%) and **7** (9%) as yellow viscous liquids and high molecular weight products. The properties of **7** were identical with those previously reported [1].

The same procedure was followed using methanol-O-d_1 as trapping agent. The reaction products were obtained in yields similar to those when methanol was the trapping agent. The ratio of axial to equatorial deuterium on the 10-carbon in **6** and **6′** was about 1/3.

For *SS*(*RR*), **6**: ^{1}H-NMR: −0.15 (s, 3H, CH_3), 0.41 [s, 9H, $C(CH_3)_3$], 1.41–1.72 (m, 3H, CH and CH_2), 3.17 (s, 3H, OCH_3), [3.66 (d, 1H, J 18.3 Hz), 4.02 (d, 1H, J 18.3 Hz) and 4.12 (d, 1H, J 7.9 Hz) (benzyl-H)] 6.96–7.43 (m, 13H, aryl-H). ^{13}C-NMR: −4.95 (Si-CH_3), 28.70 (Si-CH), 29.59 [$C(CH_3)_3$], 31.49 [$C(CH_3)_3$), 38.83 (CH_2), 36.00 and 48.35 (benzyl-carbons), 49.68 (OCH_3), 125.28, 125.39,

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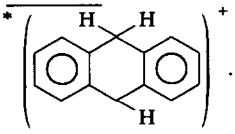
* 

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125.79, 125.85, 127.38, 127.55, 128.14, 128.73, 129.07, 134.16, 136.81, 137.31, 137.52, 140.23, 141.02 (aryl-carbons).

For *RS*(*SR*), **6′**: ^{1}H-NMR: −0.25 (s, 3H, C*H*$_3$), 0.53 [s, 9H, C(C*H*$_3$)$_3$], 1.49–1.63 (m, 1H, C*H*), 1.68–1.73 (m, 2H, C*H*$_2$) 3.09 (s, 3H, OC*H*$_3$), [3.77 (d, 1H, *J* 19.2 Hz), 4.19 (d, 1H, *J* 5.5 Hz) and 4.30 (d, 1H, *J* 19.2 Hz) (benzyl-H)], 7.01–7.44 (m, 13H, aryl-H). ^{13}C-NMR: −5.78 (Si–*C*H$_3$), 28.61 (Si–*C*H), 29.46 (C(*C*H$_3$)$_3$), 31.55 [*C*(CH$_3$)$_3$], 39.07 (*C*H$_2$), 35.92 and 47.65 (benzyl-carbons), 50.08 (O*C*H$_3$), 125.34, 125.64, 126.16, 126.85, 127.08, 127.50, 127.66, 128.58, 128.67, 129.01, 129.07, 134.03, 137.19, 140.04, 140.73 (aryl-carbons). MS *m*/*z* (relative intensity): 180 (17), 179 (100, $C_{14}H_{11}^+$), 178 (31), 151 [17, $(PhMeSiOMe)^+$], 121 [18, $(PhMeSiH)^+$], 59 (4), 57 (3). Anal. Found: C, 80.57; H, 8.07. Calc. for $C_{28}H_{34}SiO$: C, 81.10; H, 8.26%.

Photolysis of E-5 with methanol (expt. 2)

This experiment was carried out in the same manner as the above except that 97.9% of the *E*-**5** was photolyzed. Photolysis for 12 h gave 90% decomposition of *E*-**5**. Reaction products were **6** (39.9%), **6′** (13.0%) and **7** (8%) along with higher molecular weight products.

Photolysis of 6 with methanol (expt. 3)

A solution of 16.3 mg (0.039 mmol) of **6** and 40 mg (1.25 mmol) of methanol in 0.6 ml of cyclohexane was irradiated. After 12 h of irradiation GLC analysis showed 32.4% of the unchanged **6** and 21.6% of **6′**, in addition to 1.0% of the methanol-trapped silene adducts, **7**.

Photolysis of 6′ with methanol (expt. 4)

This experiment was carried out in the same manner as the above with the exception that 98.8% of the **6′** was photolyzed. After 12 h of irradiation the reaction mixture showed 32.7% of unchanged **6′**, 24.1% of **6** and 1.4% of **7**.

Acknowledgment

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References

1 P.R. Jones and M.E. Lee, J. Am. Chem. Soc., 105 (1983) 6725.
2 H. Matsumoto, T. Arai, H. Watanabe and Y. Nagai, J. Chem. Soc., Chem. Commun., (1984) 724.
3 R.B. Woodward and T. Zkatz, Tetrahedron, 5 (1959) 70; R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, 1970.
4 M.E. Lee, J.K. Lee and C.H. Kim, Bull. Kor. Chem. Soc., 8 (1987) 355.
5 P.B. Valkovich, T.I. Ito and W.P. Weber, J. Org. Chem., 39 (1974) 3543.
6 P. Jutzi and P. Langer, J. Organomet. Chem., 202 (1980) 401.
7 P. John, B.G. Gowenlock and P. Groome, J. Chem. Soc., Chem. Commun., (1981) 806.
8 P.R. Jones, M.E. Lee and L.T. Lim, Organometallics, 2 (1983) 1039.
9 A.G. Brook and J.M. Duff, J. Am. Chem. Soc., 91 (1969) 2118.
10 M.J. Michalczyk, R. West and J. Michl, Organometallics, 4 (1985) 826; M.J. Michalczyk, R. West and J. Michl, J. Am. Chem. Soc., 106 (1984) 821.