

# A Novel Stereoselective Photoinduced Intramolecular Cyclization of 1-(o-Allyloxyphenyl)-2-pentamethyldisilanyl Ethynes.

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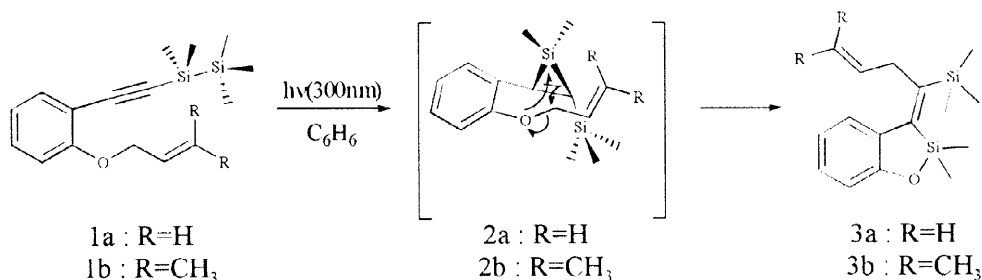
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**Abstract :** Photolysis of 1-(o-allyloxyphenyl)-2-pentamethyldisilanyl ethynes **1a** and **1b** in benzene provides novel stereoselective intramolecular cyclization products **3a** and **3b**. © 1998 Elsevier Science Ltd. All rights reserved.

Photolysis of alkynyl-substituted pentamethyldisilanes offers a convenient route to the silacycloprenes.<sup>1</sup> During the course of our investigations on the photochemical reaction pathways *via* silacycloprenene intermediates,<sup>2</sup> the photoreaction of 1-(o-allyloxyphenyl)-2-pentamethyldisilanyl ethynes **1a** and **1b** attracted our attention since a novel intramolecular reaction of allyloxy group with the photogenerated silacycloprenene is expected.

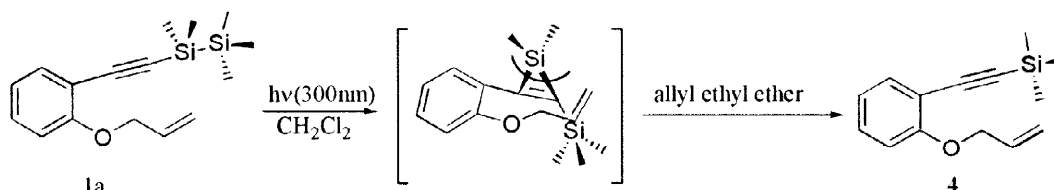
Irradiation of **1a** and **1b**<sup>3</sup> ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>) in deaerated benzene with 300nm UV light provided novel stereoselective cyclization products **3a** and **3b** (25%, 18% yield, respectively)<sup>4</sup> along with some decomposition products of unknown structure. The UV absorption spectrum of **1a** turned into that of photoproduct **3a** gradually with the irradiation time. As the absorbance at around 306 and 298nm decreased, the intensity of absorption at around 324 and 280nm increased. After irradiation of **1a** in dry methylene chloride for 5 minutes<sup>5</sup>, dry benzene was added and HPLC analysis showed the formation of the product **3a**, strongly suggesting the **2a** → **3a** rearrangement to be the thermal process. Photolysis of **1b** in dry benzene gave only the regioselective photoproduct **3b** as shown in Scheme 1.

Scheme 1



The results indicate the initial formation of silacycloprenene intermediate **2** upon irradiation

followed by the intramolecular oxygen-silicon bond formation to give the product **3** with *Z* configuration as the sole photoproduct. The stereoselective cycloaddition reaction leading to *Z* configuration indicates concerted addition of allyloxy group to silacyclopropene formed. After the photolysis of **1a** in dry methylene chloride for 5 minutes, allyl ethyl ether was added to check the thermal intermolecular reaction of the allylic ether with the silacyclopropene intermediate formed. No intermolecular reaction product was formed but only 1-(*o*-allyloxyphenyl)-2-trimethylsilylethyne **4**<sup>6</sup> was obtained.



The structure of the photoproduct **3a** was determined by various physical methods including <sup>1</sup>H-<sup>1</sup>H and <sup>1</sup>H-<sup>13</sup>C correlation spectroscopy (COSY), HMBC, nuclear Overhauser and exchange spectroscopy (NOESY) (Table 1). The 3D-structure of **3a** was determined by NOESY spectrum. In particular, the presence of the cross-peaks between a proton of C(3) and the protons of C(7) and C(12) and between a proton of C(12) and the protons of C(13) showed the close proximity of a proton of C(3) to the protons of C(7) and C(12) and a proton of C(12) to the protons of C(13), indicating that these protons are located on the same surface of the molecule. The location of the quaternary carbons was identified by the HMBC spectrum. The presence of the cross-peaks due to the vicinal coupling between the protons of C(7), C(3), C(13) and the quaternary carbon C(5) showed the connectivity of the carbon C(5) and the benzene ring, dimethylsilyl group, and carbon C(4). In the same manner, the connectivity of the carbon C(4) and allyl group and trimethylsilyl group was established. The skeletal structure of **3a** was established as shown in Figure 1.

Further studies are in progress to elucidate the more detailed mechanism of the reaction.

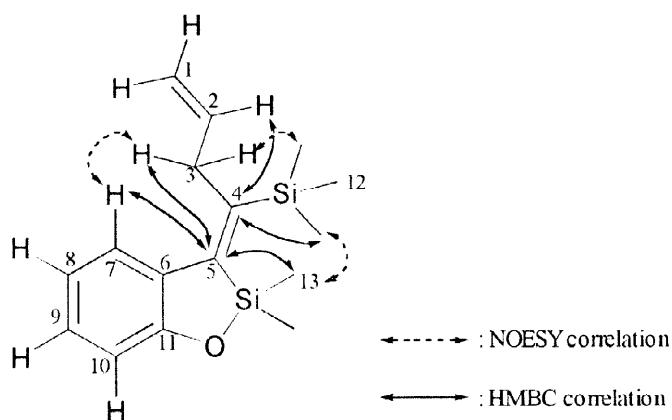


Figure 1. Important correlations observed in HMBC and NOESY spectra of photoproduct **3a**.

Table 1.  $^1\text{H}$  NMR(500MHz) and  $^{13}\text{C}$  NMR(125MHz) data for photoproduct **3a** in  $\text{CDCl}_3$ \*

Position	$\delta_{\text{C}}(\text{ppm})$	$\text{M}^{\oplus}$	$\delta_{\text{H}}(\text{ppm})$	$\text{I}^{\dagger}$	$\text{M}^{\star}$	$J_{\text{H-H}}(\text{Hz})$	NOESY
1 <sub>a</sub>	116.40	t	5.08	1H	dq	17.6( $J_{1\alpha\text{H}-2\text{H}}$ ), 2.0( $J_{1\alpha\text{H}-3\text{H}}$ , $J_{1\beta\text{H}}$ )	
1 <sub>b</sub>	116.40	t	5.15	1H	dq	10.3( $J_{1\beta\text{H}-2\text{H}}$ ), 2.0( $J_{1\beta\text{H}-3\text{H}}$ , $J_{1\alpha\text{H}}$ )	2H
2	135.66	d	6.01	1H	m		1H, 3H
3	38.34	t	3.41	2H	dt	4.9( $J_{3\text{H}-2\text{H}}$ ), 2.0( $J_{3\text{H}-1\text{H}}$ )	7H <sup>**</sup> , 12H <sup>**</sup> , 2H
4	153.01	s					
5	147.41	s					
6	130.58	s					
7	127.59	d	7.59	1H	dd	7.8( $J_{7\text{H}-8\text{H}}$ ), 1.5( $J_{7\text{H}-9\text{H}}$ )	8H, 3H <sup>**</sup>
8	119.83	d	6.82	1H	td	7.8( $J_{8\text{H}-7\text{H}}$ ), 1.5( $J_{8\text{H}-10\text{H}}$ )	9H, 7H
9	129.36	d	7.14	1H	td	7.8( $J_{9\text{H}-8\text{H}}$ ), 1.5( $J_{9\text{H}-7\text{H}}$ )	8H, 10H
10	115.27	d	6.88	1H	dd	7.8( $J_{10\text{H}-9\text{H}}$ ), 1.5( $J_{10\text{H}-8\text{H}}$ )	9H
11	160.00	s					
12	0.48	q	0.209	3H	s <sup>‡</sup>		13H <sup>**</sup> , 3H <sup>**</sup>
12	0.50	q	0.214	3H	s		13H <sup>**</sup> , 3H <sup>**</sup>
12	0.51	q	0.221	3H	s		13H <sup>**</sup> , 3H <sup>**</sup>
13	1.17	q	0.54	6H	s		12H <sup>**</sup>

\* All these assignments were confirmed by  $^1\text{H}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{13}\text{C}$  COSY and NOESY, HMBC spectra.

‡ Multiplicities were determined by DEPT spectrum.

‡ Integrated intensity.

♦ Multiplicities.

\*\* Important correlations by NOESY spectrum.

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- 1a** : Colorless oil ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ , 200MHz)  $\delta_{\text{H}}$  0.15(9H, s), 0.25(6H, s), 4.57(2H, dt,  $J=4.8$ , 1.6Hz), 5.30(1H, dq,  $J=7.4$ , 1.5Hz), 5.48(1H, dq,  $J=17.2$ , 1.6Hz), 6.03(1H, m), 6.86(2H, m), 7.22 (1H, td,  $J=7.7$ , 1.7Hz), 7.40(1H, dd,  $J=7.5$ , 1.7Hz) ;  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 50MHz)  $\delta_{\text{C}}$  159.48, 133.85, 133.04, 129.56, 120.53, 117.09, 113.39, 112.40, 103.30, 97.49, 69.17, -2.51, -2.94 ; UV( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  306, 298, 261nm ; FT-IR (NaCl) 2953.0, 2151.9, 1488.7, 1246.5, 749.4  $\text{cm}^{-1}$  ; MS (70eV)  $m/z$  288 ( $\text{M}^+$ ) ; HRMS ( $\text{M}^+$ ) calcd for  $\text{C}_{16}\text{H}_{24}\text{OSi}_2$  288.1366, found 288.1352.

- 1b** : Colorless oil ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ , 300MHz)  $\delta_{\text{H}}$  0.16(9H, s), 0.26(6H, s), 1.72(3H, s), 1.77(3H, s), 4.56(2H, d,  $J=6.6\text{Hz}$ ), 5.50(1H, t,  $J=6.6\text{Hz}$ ), 6.85(2H, m), 7.23(1H, td,  $J=7.9$ , 1.8Hz), 7.40(1H, dd,  $J=7.9$ , 1.8Hz) ;  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75MHz)  $\delta_{\text{C}}$  160.03, 137.43, 133.95, 129.63, 120.30, 120.03, 113.39, 112.50, 103.53, 97.29, 65.60, 25.64, 18.15, -2.70, -3.11 ; UV( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  307, 299, 261nm ; FT-IR (NaCl) 2952.2, 2151.8, 1488.0, 1246.9, 749.1  $\text{cm}^{-1}$  ; MS (70eV)  $m/z$  316( $\text{M}^+$ ) ; HRMS ( $\text{M}^+$ ) calcd for  $\text{C}_{18}\text{H}_{28}\text{OSi}_2$  316.1679, found 316.1654.
4. **3a** : Colorless oil ; UV( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  324, 280, 273nm ; FT-IR (NaCl) 2956.8, 1594.9, 1252.3, 751.7  $\text{cm}^{-1}$  ; MS (70eV)  $m/z$  288( $\text{M}^+$ ) ; HRMS ( $\text{M}^+$ ) calcd for  $\text{C}_{16}\text{H}_{24}\text{OSi}_2$  288.1366, found 288.1367.
- 3b** : Colorless oil ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ , 300MHz)  $\delta_{\text{H}}$  0.20(9H, s), 0.51(6H, s), 1.68(3H, d,  $J=0.9\text{Hz}$ ), 1.75(3H, d,  $J=1.5\text{Hz}$ ), 3.30(2H, d,  $J=4.2\text{Hz}$ ), 5.07(1H, m), 6.82(1H, td,  $J=7.9$ , 1.5Hz), 6.87(1H, dd,  $J=7.9$ , 1.5Hz), 7.13(1H, td,  $J=7.9$ , 1.5Hz), 7.52(1H, dd,  $J=7.9$ , 1.5Hz) ;  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75MHz)  $\delta_{\text{C}}$  160.14, 156.54, 145.70, 133.33, 131.01, 129.14, 128.06, 123.35, 119.87, 115.25, 33.84, 25.56, 18.18, 1.00, 0.29 ; UV( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  323, 280, 273 nm ; FT-IR (NaCl) 2964.1, 1595.1, 1251.4, 751.5  $\text{cm}^{-1}$  ; MS (70eV)  $m/z$  316( $\text{M}^+$ ) ; HRMS ( $\text{M}^+$ ) calcd for  $\text{C}_{18}\text{H}_{28}\text{OSi}_2$  316.1679, found 316.1679.
5. In the photoreaction of **1a** in dry methylene chloride, no photocycloproduct **3a** was observed but the silacyclopentene intermediate is formed. After irradiation of **1a** ( $5 \times 10^{-4} \text{mol dm}^{-3}$ ) in 5ml of methylene chloride for 5 minutes, 5ml of methanol was added and detected methanol addition to silacyclopentene by HPLC. The results strongly support the formation of silacyclopentene intermediate. When acetone was added as a nucleophile, the acetone addition products were obtained. The photolysis of **1a** in the presence of nucleophiles such as methanol or acetone will be reported elsewhere.
6. **4** : Colorless oil ;  $^1\text{H}$  NMR( $\text{CDCl}_3$ , 300MHz)  $\delta_{\text{H}}$  0.26(9H, s), 4.60(2H, dt,  $J=4.6$ , 1.6Hz), 5.30(1H, dq,  $J=10.6$ , 1.6Hz), 5.56(1H, dq,  $J=17.2$ , 1.7Hz), 6.05(1H, m), 6.88(2H, m), 7.26(1H, td,  $J=7.7$ , 1.7Hz), 7.44(1H, dd,  $J=7.6$ , 1.7Hz) ;  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75MHz)  $\delta_{\text{C}}$  159.94, 134.24, 133.29, 130.23, 121.00, 117.23, 112.77, 101.61, 98.97, 96.82, 69.43, 0.45 ; UV( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  304, 296, 260nm ; FT-IR (NaCl) 2959.4, 2158.8, 1489.2, 1250.5, 751.88  $\text{cm}^{-1}$  ; MS (70eV)  $m/z$  230( $\text{M}^+$ ) ; HRMS ( $\text{M}^+$ ) calcd for  $\text{C}_{14}\text{H}_{18}\text{OSi}$  230.1127, found 230.1079.
7. The  $^1\text{H}$  NMR signal due to  $\text{SiMe}_3$  group appeared as three lines because the NMR time scale in 500MHz spectrometer is fast enough to detect the C(12) methyl groups as the different peaks.