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

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Abstract : Photolysis of 1-(o-allyloxyphenyl)-2-pentamethyldisilanyl ethynes1a 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 silacyclopropenes.¹ During the course of our investigations on the photochemical reaction pathways *via* silacyclopropene intermediates,² 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 silacyclopropene is expected.

Irradiation of 1a and 1b³ ($5x10^{-4}$ mol dm⁻³) in deaerated benzene with 300nm UV light provided novel stereoselective cyclization products 3a and 3b (25%, 18% yield, respectively)⁴ 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 minutes⁵, dry benzene was added and HPLC analysis showed the formation of the product 3a, strongly suggesting the $2a \rightarrow 3a$ rearrangement to be the thermal process. Photolysis of 1b in dry benzene gave only the regioselective photoproduct 3b as shown in Scheme 1.



The results indicate the initial formation of silacyclopropene 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**⁶ was obtained.



The structure of the photoproduct **3a** was determined by various physical methods including ¹H-¹H and ¹H-¹³C 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.

Position	ծ _e (ppm)	M [◊]	δ _н (ppm)	1ţ	M*	 Ј _{Н-Н} (Н <i>х</i>)	NOESY
lα	116.40	t	5.08	IH	dq	17.6(J _{10H 2H}), 2.0(J _{10H-34 1BH})	
1 3	116.40	1	5.15	ıн	dq	$10.3(J_{1011-211}), 2.0(J_{1011-341, 1041})$	2H
2	135,66	d	6 01	іН	m		1H, 3H
3	38,34	t	3,41	2H	dt	$4.9(J_{3B-2H}), 2.0(J_{3B-0H})$	7H**, 12H**, 2H
4	153.01	s					
5	147.41	s					
6	130,58	s					
7	127 59	d	7.59	1H	dd	7 8(J _{2H-80}), 1 5(J _{2H-9R})	8H, 3H
8	119.83	d	6,82	ìН	td	7.8(J _{8H-1011}), 1.5(J _{8H-1011})	9H. 7H
9	129.36	d	7.14	1H	td	7.8($J_{01,81}$, 1.5($J_{01,71}$)	8H, 10H
10	115 27	d	6.88	1H	dd	$7.8(J_{10H-911}), 1.5(J_{10H-8H})$	9H
11	160,00	s					
12	0.48	q	0.209	3H	ร้		13H ^{**} , 3H ^{**}
12	0.50	q	0.214	3H	S		13H ^{**} , 3H ^{**}
12	0.51	q	0.221	3H	5		13H ^{**} , 3H ^{**}
13	1.17	q	0.54	6H	5		12H**

Table 1.¹H NMR(500MHz) and ¹³C NMR(125MHz) data for photoproduct 3a in CDCL³

* All these assignments were confirmed by 'H-'H and 'H-'C COSY and NOESY, HMBC spectra

P Multiplicities were determined by DEPT spectrum

‡ Integrated intensity

Multiplicities.

** Important correlations by NOESY spectrum.

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- 3. **1a** : Colorless oil ; ¹H NMR(CDCl₃, 200MHz) δ_{11} 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); ¹³C NMR(CDCl₃, 50MHz) δ_{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(CH₂Cl₂) λ_{max} 306, 298, 261*nm*; FT-IR (NaCl) 2953.0, 2151.9, 1488.7, 1246.5, 749.4 *cm*⁻¹; MS (70*eV*) *m z* 288 (M⁺); HRMS (M⁺) calcd for C₁₆H₂₄OSi₂ 288.1366, found 288.1352.

- **1b** : Colorless oil ; ¹H NMR(CDCl₃, 300MHz) δ_{II} 0.16(9H, s), 0.26(6H, s), 1.72(3H,s), 1.77(3H,s), 4.56(2H, d, J=6.6Hz), 5.50(1H, t, J=6.6Hz), 6.85(2H, m), 7.23(1H, td, J=7.9, 1.8Hz), 7.40(1H, dd, J=7.9, 1.8Hz); ¹³C NMR(CDCl₃, 75MHz) δ_{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(CH₂Cl₂) λ_{max} 307, 299, 261*nm*; FT-IR (NaCl) 2952.2, 2151.8, 1488.0, 1246.9, 749.1 *cm*⁻¹; MS (70*eV*) *m z* 316(M⁺); HRMS (M⁺) calcd for C₁₈H₂₈OSi₂ 316.1679, found 316.1654.
- 4. **3a** : Colorless oil ; UV(CH₂Cl₂) λ_{max} 324, 280, 273*nm* ; FT-IR (NaCl) 2956.8, 1594.9, 1252.3, 751.7*cm*⁻¹ ; MS(70*eV*)*m*:*z* 288(M⁺) ; HRMS (M⁺) calcd for C₁₆H₂₄OSi₂ 288.1366, found 288.1367.
 - **3b** : Colorless oil ; ¹H NMR(CDCl₃, 300MHz) δ_{11} 0.20(9H, s), 0.51(6H, s), 1.68(3H, d, J=0.9Hz), 1.75(3H, d, J=1.5Hz), 3.30(2H, d, J=4.2Hz), 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); ¹³C NMR(CDCl₃, 75MHz) δ_{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(CH₂Cl₂) λ_{max} 323, 280, 273 nm ; FT-IR (NaCl) 2964.1, 1595.1, 1251.4, 751.5cm⁻¹; MS (70eV) m z 316(M⁺) ; HRMS (M⁺) calcd for C₁₈H₂₈OSi₂ 316.1679, found 316.1679.
- 5. In the photoreaction of 1a in dry methylene chloride, no photocycloproduct 3a was observed but the silacyclopropene intermediate is formed. After irradiation of 1a (5 x 10⁻⁴mol dm⁻³) in 5ml of methylene chloride for 5 minutes, 5ml of methanol was added and detected methanol addition to silacyclopropene by HPLC. The results strongly support the formation of silacyclopropene 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 ; ¹H NMR(CDCl₃, 300MHz) δ_{11} 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) ; ¹³C NMR(CDCl₃, 75MHz) δ_{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(CH₂Cl₂) λ_{max} 304, 296, 260*nm*; FT-IR(NaCl) 2959.4, 2158.8, 1489.2, 1250.5, 751.88*cm*⁻¹; MS (70*eV*) *m*·z 230(M⁺) ; HRMS (M⁺) calcd for C₁₄H₁₈OSi 230.1127, found 230.1079.
- 7. The ¹H NMR signal due to SiMe₃ 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.