Photoreaction *via* Non-Resonant Two-Photon Excitation. Selective Silylene Extrusion from 2,2-Diphenyltrisilane

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Non-resonant two-photon excitation of 2,2-diphenylhexamethyltrisilane with a 532 nm pulsed laser light induced the two major reactions, silylene extrusion and migration of the β-trimethylsilyl group with a quite different selectivity from that for the single-photon excitation.

Recent spectroscopic studies have shown that a number of molecules have the low-lying electronic excited states[1] to which the non-resonant two-photon (NRTP) absorption is allowed, while the direct single-photon absorption is forbidden, as first predicted by Göppert-Mayer.[2] However, no study has been reported on the photochemical reactions induced by NRTP excitation of the molecules in the condensed phases to date. We have found the first example of photoreactions induced by NRTP in solution.[3] Thus, irradiation of a hexane solution of 2,2-diphenylhexamethyltrisilane (**1** in Scheme I) with a 532 nm light (second harmonic of a pulsed Nd:YAG laser) at room temperature gave two types of photo-products [**2** and **3** (= **3A** + **3B**)] in the presence of excess ethanol, although **1** showed no absorption at longer wavelengths than 300 nm ($\varepsilon < 0.5$, Figure 1). The product yields increased in proportion to the square of the laser intensity. In addition, the ratio **2**/**3** was quite different from that induced by the single-photon absorption of a 266 nm light (fourth harmonic of the Nd:YAG laser). The NRTP method may offer a promising technique to control photochemical reaction pathways in condensed systems at ambient temperatures by using a conventional laser system.

Whereas **1** is a well-known photochemical precursor of diphenylsilylene (Path A in Scheme I),[6] a 1,3-silyl migration (Path B) is usually a major side reaction. Actually, photolysis of a hexane solution of **1** ($1.1\mathrm{x}10^{-2}$ M) in the presence of ethanol (1 M) with a 32-W low-pressure Hg lamp gave **2** and **3** in 50 and 37 % yields, respectively, with consumption of 24% of **1**.[7] The product yields did not change seriously up to 70% conversion. A similar product distribution was obtained under irradiation with a pulsed 266 nm laser light (17.5 MW/cm^2, 5ns, 10 Hz); the yields of **2** and **3** were 53 and 30%, respectively, with consumption of 30% of **1**. The quantities of **1**, **2**, and **3** were determined by means of gas chromatography.

When **1** was irradiated with a pulsed 532 nm laser light (212 MW/cm^2, 6 ns, 10 Hz) for 1 h under otherwise the same conditions as above, **2** and **3** were obtained in 80 and 13% yields, respectively, with consumption of 20 % of **1**. The yield of **2** increased in proportion to the square of the laser intensity as shown in Figure 2, being indicative of the two-photon nature of the reaction. The irradiation of an intense IR light pulse (fundamental light of the Nd:YAG laser; 1064 nm, 120 MW/cm^2, 8 ns, 10 Hz) for 1 h induced no reaction of **1**. Therefore, the observed reaction is not caused by heating effects during irradiation. Since the product yield increased proportionally with the irradiation time, no secondary photoreactions of the silylene are involved.

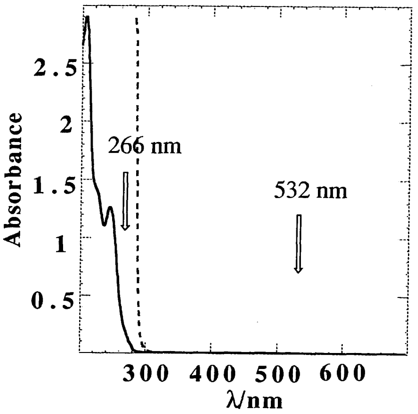
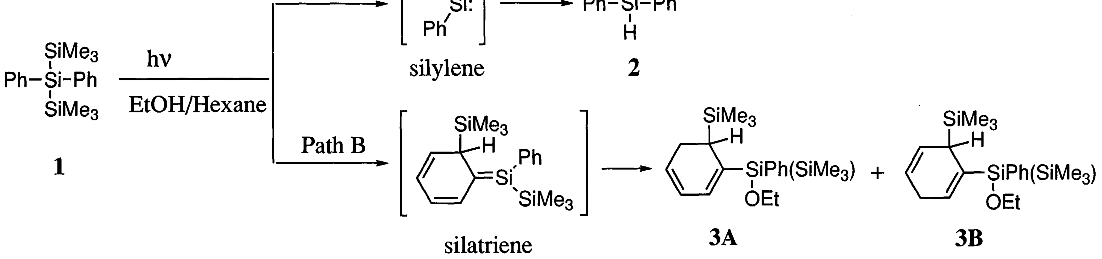


Figure 1. Absorption spectra of **1** in hexane: c = 7.49x10^{-5} M (——); c = 7.31x10^{-3} M (--------). Arrows denotes wavelengths of laser lights, 266 and 532 nm, for excitation.

Scheme I



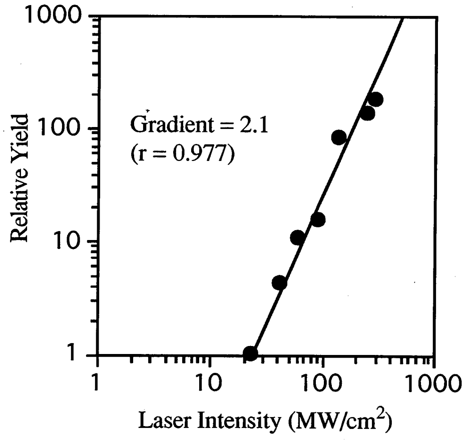


Figure 2. A log-log plot of the yield of **2** against light intensity under irradiation of **1** with the 532 nm light for 1 h. The laser power was attenuated by using a halfwave plate and a Glan polarizer. The yield at the light intensity of 24.3 MW/cm^2 was taken as unity.

The characteristic feature of the photoreactions induced by the NRTP is the selectivity of the reaction pathways. The product ratio (**2**/**3**) of 80/13 by the NRTP is much higher than that by the irradiation of the 266 nm light (53/30). The NRTP highly favors path A to path B.

The present NRTP results may suggest that two non-polar excited states, E_1 and E_2, which are close in energy but distinguished by symmetry, are responsible for the paths A and B, respectively (see Figure 3). Since the NRTP absorption obeys the different selection rule from direct single-photon absorption, the population of E_1 and E_2 at the initial stage of the reaction may be different between these two absorption modes, even if the same energy is given to a molecule by these processes. This may be the origin of the selectivity difference. Because of the rapid internal conversion to the lowest excited states, selectivity control of the photoreactions by control of the nature of the excitation process is considered in general not to be feasible (Kasha's rule).[8] The above explanation apparently contradicts the Kasha's rule. Whereas further works should be performed to elucidate the origin of the observed selectivity, the NRTP method is highly promising as a new technique for controlling the photoreaction.[9]

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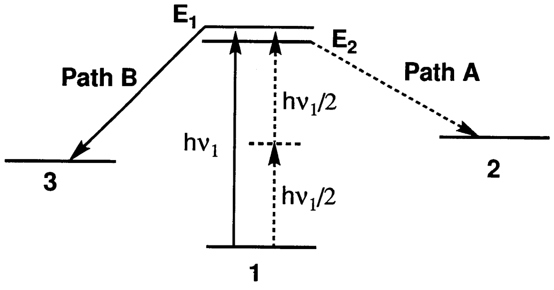

Figure 3. Schematic representation of selective photoreactions via NRTP.

References and Notes

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1 For some recent examples, see: R. L. Swofford and W. M. McClain, *J. Chem. Phys.*, **59**, 5740 (1973); G. R. Holtom, W. M. McClain, *Chem. Phys. Lett.*, **44**, 436 (1976); T. M. Stachelek, T. A. Pazoha, W. M. McClain and R. P. Drucker, *J. Chem. Phys.*, **66**, 4540 (1977); H. L. B. Fang, R. J. Thrash and G. E. Leroi, *Chem. Phys. Lett.*, **57**, 59 (1978); H. L. B. Fang, R. J. Thrash and G. E. Leroi, *J. Chem. Phys.*, **67**, 3389 (1977).

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3 Although a number of studies of the photochemistry via sequential multiphoton absorption have been reported until now,[4] the non-resonant multi-photon reactions have only been observed spectroscopically with the multi-photon ionization method[5] in gas phase.

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7 **2**: ^{1}H NMR (300.1 MHz, acetone-*d*$_6$) δ 7.64-7.61 (m, 4), 7.47-7.42 (m, 6), 5.40 (s, 1), 3.85 (q, J = 7.0 Hz, 2), 1.22 (t, J = 7.0 Hz, 3); ^{13}C NMR (75.4 MHz, acetone-*d*$_6$) δ 135.2, 135.0, 131.2, 128.9, 61.0 18.4; ^{29}Si NMR (59.6 MHz, acetone-*d*$_6$) δ -12.5; Anal. Calcd for $C_{14}H_{16}OSi$: C, 73.63; H, 7.06. Found: C, 73.45; H, 6.75. The compounds **3A** and **3B** were isolated as a mixture (**3A**/**3B** = 1.4) by preparative glc. Since each of them is composed of two diastereomers, the ^{1}H NMR (300.1 MHz, C_6D_6) spectrum of the mixture was rather complicated. The following are the NMR data for **3A** and **3B** except for the aromatic region [δ 7.83-7.20 (m)]. **3A**: δ 6.30-6.26 (m, 1), 6.25-6.20 (m, 1), 5.78-5.72 (m, 1), 3.79 and 3.78 (two q, 2, J = 6.9 Hz), 2.54-2.42 (m, 1), 2.20-2.09 (m, 1), 1.55-1.48 (m, 1), 1.23 and 1.22 (two t, 3, J = 6.9 Hz), 0.30 and 0.29 (two s, 9), 0.02 and 0.01 (two s, 9). **3B**: δ 6.36-6.33 (m, 1), 5.89-5.83 (m, 1), 5.62-5.56 (m, 1), 3.81 (q, 2, J = 6.9 Hz), 2.77-2.69 (m, 2), 2.64-2.58 (m, 1), 1.23 (t, 3, J = 6.9 Hz), 0.23 (s, 9), 0.09 (s, 9); HRMS for a mixture of **3A** and **3B** *m/z* Found 374.1912, Calcd for $C_{20}H_{34}OSi_3$ 374.1918.

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