Nanosecond Laser Flash Photolysis and Steady-State Photolysis Studies of Benzyltrimethylsilane and Trimethylsilyldiphenylmethane

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Photophysical and photochemical processes of benzyltrimethylsilane and trimethylsilyldiphenylmethane have been studied by fluorescence measurements and by steady-state and nanosecond laser flash photolyses. A remarkable solvent effect was observed for the laser flash photolysis of benzyltrimethylsilane; in methanol, absorption bands due to benzyl-type radicals and the triplet were observed, while in cyclohexane, only T−T absorption was observed. On the other hand, no solvent effect was observed for the laser flash photolysis of trimethylsilyldiphenylmethane; a transient absorption attributable to the 1,3-trimethylsilyl-shifted intermediate was observed with a lifetime of ca. 27 ms in both solvents, and no absorption band ascribable to diphenylmethyl radicals or the triplet was observed. GC-MS spectra of photoproducts resulting from trimethylsilyldiphenylmethane were consistent with the assignment of the transient absorption. These results were explained in terms of the calculated molecular structure for the excited singlet states of these molecules by the PM3 method.

Introduction

A number of photochemical studies of aromatic silicon compounds have been performed in these 2 decades. Benzyltrimethylsilane is one of fundamental aromatic silicon compounds and has sometimes been used as an electron donor in the study of electron-transfer reactions[1−6] because of its low ionization potential.[7] Nanosecond laser flash photolysis of benzylsilane derivatives in the presence of nucleophilic reagent has been studied by the excitation of the electron acceptor,[3] and it has been shown that rapid fragmentation of radical cations of benzylsilanes produced by electron transfer takes place to give benzyl radicals in acetonitrile.

There have been, however, few reports on the study of direct photolysis of benzylsilanes.[1,2,8,9] Valkovich et al.[1] studied the direct photolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane in degassed methan-[^{2}H]-ol at 0 °C and obtained 3-phenyl-[3-^{2}H$_1$]-propyldimethylmethoxysilane in quantitative yield. They proposed that cleavage of the Si−C (benzyl) bond took place to form a zwitterion in which the benzyl carbon is negatively charged and the silyl group is positively charged. Kira et al. studied the photolysis of benzyltrimethylsilane and its derivative in benzene at room temperature by analyzing the photoproducts and elucidated the reaction by considering the formation of a pair of benzyl radical and silyl radical in the solvent cage.[8] They also reported that 1,3-isomerization took place to produce *ortho*-tolyltrimethylsilane with an efficiency of 2%.

In a previous paper we studied the photophysical process of benzyltrimethylsilane and reaction intermediates produced upon the photolysis at 77 K in glassy matrices.[9] It was shown that benzyl radicals were predominantly produced upon the direct excitation of benzyltrimethylsilane in methanol (MeOH) or ethanol (EtOH) glass, while in 3-methylpentane (3MP) glass, α-trimethylsilylbenzyl radicals were biphotonically formed via the lowest triplet state. This kind of solvent effect has not been observed for the photolysis of its carbon analogue, neopentylbenzene, or toluene. The predominant formation process of benzyl radicals in the photolysis of benzyltrimethylsilane has been considered to be nucleophilic reaction in the deformed excited singlet state predicted by the PM3 calculation or in a higher triplet state with alcohol.

To the best of our knowledge, laser flash photolysis of benzyltrimethylsilane (**1**) or trimethylsilyldiphenylmethane (**2**) with direct excitation has never been studied. In this paper, to clarify the photochemical reaction mechanism of benzylsilanes at room temperature, nanosecond laser flash photolysis has been studied for benzyltrimethylsilane and trimethylsilyldiphenylmethane in comparison with the results of the steady-state photolysis at 77 K and GC-MS analysis of photoproducts. Photophysical process has also been studied by fluorescence measurements.

Experimental Section

Benzyltrimethylsilane (**1**) (Shin-Etsu Silicone Chemical Co.) was purified by distillation under Ar gas, and its purity was confirmed by fluorescence measurements. Trimethylsilyldiphenylmethane (**2**) was synthesized by Grignard reaction as follows. The mixed solution of chlorotrimethylsilane (0.30 mol) and bromodiphenylmethane (0.10 mol) in 50 mL tetrahydrofuran (THF) was dropped to 300 mL THF solution containing magnesium turnings (0.40 mol) with stirring under Ar gas atmosphere. The reaction was stopped by adding water and the organic layer was extracted with *n*-hexane. After evaporation of solvent, the residue was recrystallized three times from cyclohexane. Formation and purity of **2** was confirmed by GC-MS and fluorescence measurements.

Toluene (Tokyo Chemical Co., SG) and 2,3-dimethyl-1,3-butadiene (Aldrich Chemical Co., 98%) were used as received.

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3-Methylpentane (Wako Pure Industries Ltd., GR) was purified by distillation over $LiAlH_4$ under Ar gas. 2-Chlorobutane (Tokyo Chemical Co., GR) was purified by distillation under Ar gas. Methanol (99.8% Kanto Chemical Co.), ethanol (Kanto Chemical Co., Sp.Gr), 2-propanol (99.5% Kanto Chemical Co.), 2-butanol (99.0% Kanto Chemical Co.), 1-butyronitrile (Tokyo Chemical Co.,GR), and cyclohexane (99.5% Kanto Chemical Co.) were used without further purification. Naphthalene (Tokyo Chemical Co., Zone refined Gr.) was used as received. Chlorotrimethylsilane (Kanto Chemical Co.), bromodiphenylmethane (Wako Pure Industries Ltd.), magnesium turnings (Kishida Chemical Co., for Grignard reaction), tetrahydrofuran (Kanto Chemical Co., GR), and *n*-hexane (Kanto Chemical Co., GR) were used as received.

Absorption spectra were recorded on a Hitachi U3300 spectrophotometer. Fluorescence emission and excitation spectra were measured using a Hitachi M850 fluorescence spectrometer with a band-pass of 3 nm for both excitation and emission. Fluorescence lifetimes were measured by using an Edinburgh Analytical Instruments Fl900CDL spectrometer system (H_2 pulser, pulse width 0.8 ns, 10^8 photons/pulse, repetition rate 40 kHz). Phosphorescence decay was recorded on a Hitachi M850 fluorescence spectrometer. Steady-state photolysis was carried out at 77 K using light outputs of a 100 W low-pressure mercury lamp (253.7 nm) or outputs from an Nd^{3+}:YAG laser (266 nm). A liquid nitrogen cryostat (Oxford DN-1704) and temperature controller (Oxford ITC-1) were used for measurements at various temperatures between 77 and 150 K.

Transient absorption spectra were measured by using a Unisoku TSP601H nanosecond laser photolysis system at room temperature using an Nd^{3+}: YAG laser (266 nm; outputs of fourth harmonic, pulse width 3 ns, 3 mJ/pulse, repetition rate 10 Hz, Quanta-Ray GCR-130, Spectra-Physics), a Xe lamp (500W, Ushio UI-502Q), and an oscilloscope (Gould 4090). Sample solutions were flowed at a rate of 8 mL/min through a flow cell of which the light path length was 10 mm. All samples were fully bubbled with high purity Ar or O_2 gas just before use. A chemical actinometer of tris(oxalato)ferrate(III) was used to determine the formation yields of benzyl radicals and diphenylmethyl radicals at 77 K.

Photoproducts were analyzed by use of a GC-MS spectrometer (mass selective detector 5972, gas chromatograph 5890; Hewlett-Packard, Inc.) under the condition of 16 °C/min from 150 °C. Semiempirical molecular orbital calculations (the PM3 method; MOPAC/97 version)[10] were carried out to obtain an optimized molecular structure and to estimate heat of formation of the ground and excited states of **1** and **2** and also of possible reaction intermediates and photoproducts. CNDO/S-CI calculations were performed to study the electronic spectra of **1** and **2** for the optimized geometry determined by the PM3 method.

Results and Discussion

Photophysical Parameters of Benzylsilanes. Parts a−c of Figure 1 show the absorption spectra of toluene, benzyltrimethylsilane (**1**), and trimethylsilyldiphenylmethane (**2**) in cyclohexane (CH) at room temperature, respectively. These are well explained by the results of CNDO/S-CI calculations for these compounds as shown by sticks: the structured bands around 260 nm are assigned to the $^1L_b \leftarrow ^1A$ ($^1B_2 \leftarrow ^1A_1$ in Mulliken notation) transition, and the intense short-wavelength bands are attributed to the $^1L_a \leftarrow ^1A$ ($^1B_1 \leftarrow ^1A_1$) transition. It is noted that the ^1L_a band of **2** is shifted to the red compared with that of toluene or **1** and comes closer to the ^1L_b band. In Figure 1 are shown the absorption (full line), fluorescence emission (broken line), and excitation spectra (dotted line) of toluene, **1** and **2** in CH at room temperature, respectively. Similar spectra were observed in EtOH and MeOH. Fluorescence emission spectra observed upon the excitation at 250 nm are similar to each other, though the fluorescence intensity of **2** is much weaker than the others. All fluorescence excitation spectra determined by monitoring the fluorescence at 300 nm (broken line) are similar to the corresponding absorption spectra. Parts a−c of Figure 2 show the absorption (full line), emission (broken line), and excitation spectra (dotted line) of toluene, **1** and **2** in 3-methylpentane (3MP) at 77 K. These absorption spectra are similar to those observed at room temperature, though each ^1L_a band is blue-shifted compared with that at room temperature. Upon excitation at 250 nm, fluorescence emission was observed around 280 nm with vibrational structure, and phosphorescence spectra were observed in the region of wavelengths longer than 345 nm. Excitation spectra observed by monitoring the emission at 300 nm are very similar to the absorption spectra. A good mirror-image relationship between the absorption and fluorescence spectra is confirmed for each of the samples, as shown in Figure 2. Therefore, the molecular structure of the fluorescing state is considered to be similar to that of the ground state. When phosphorescence emission was monitored at the 385-nm peak, essentially the same excitation spectra were observed with the fluorescence excitation spectra.

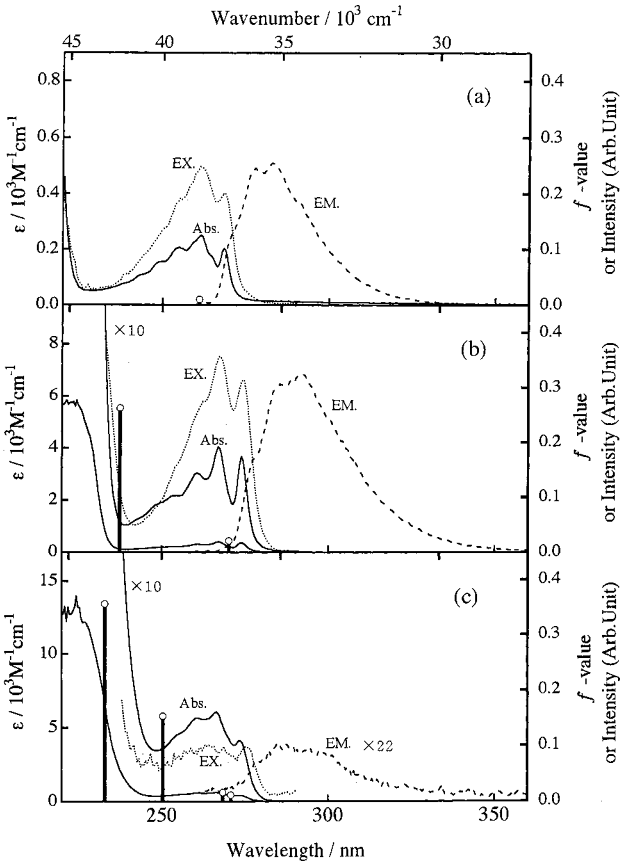


Figure 1. Calculated electronic spectra (sticks) and observed absorption spectra (full line) of toluene (a), benzyltrimethylsilane (b), and trimethylsilyldiphenylmethane (c) in cyclohexane at room temperature. Fluorescence emission (broken line) observed upon excitation at 250 nm and excitation spectra (dotted line) monitored at 300 nm are also shown.

Emission quantum yields of **1** and **2** were determined relative to that of toluene by the excitation at 250 nm. Fluorescence quantum yields of **2** (Φ_{f2}) in 3MP and EtOH at 77 K were estimated to be 0.23 ± 0.01 and 0.20 ± 0.02, respectively, the

TABLE 1: Photophysical Parameters of Fluorescence of Benzyltrimethylsilane and Trimethylsilyldiphenylmethane at 77 K and at Room Temperature[a]

sample	solvent	temperature	fluorescence quantum yield Φ_f	fluorescence lifetime τ_f/ns	radiative rate constant $k_f^0/10^6\ s^{-1}$	nonradiative rate constant $k_{nr}/10^7\ s^{-1}$
toluene	CH	rt	0.14[b]	34	4.1	2.8
	MeOH	rt	0.13[c]	24	5.8	3.6
	3MP	77 K	0.29[b]	66	4.7	1.1
	EtOH	77 K	0.27[c]	58	4.4	1.3
benzyltrimethylsilane	CH	rt	0.17	21	7.2	3.3
	MeOH	rt	0.12	19	6.3	4.6
	3MP	77 K	0.31	34	9.1	2.0
	EtOH	77 K	0.19	29	6.7	2.9
trimethylsilyldiphenylmethane	CH	rt	<0.01	<0.20	11.8[d]	226<
	MeOH	rt	<0.01	<0.26	10.2	231<
	3MP	77 K	0.23	25	9.2	3.1
	EtOH	77 K	0.20	22	9.1	3.6

[a] Error, ±15%. [b] In MP (ref 11a). [c] In EtOH (ref 11b). [d] Estimated by the Strickler−Berg equation (ref 13).

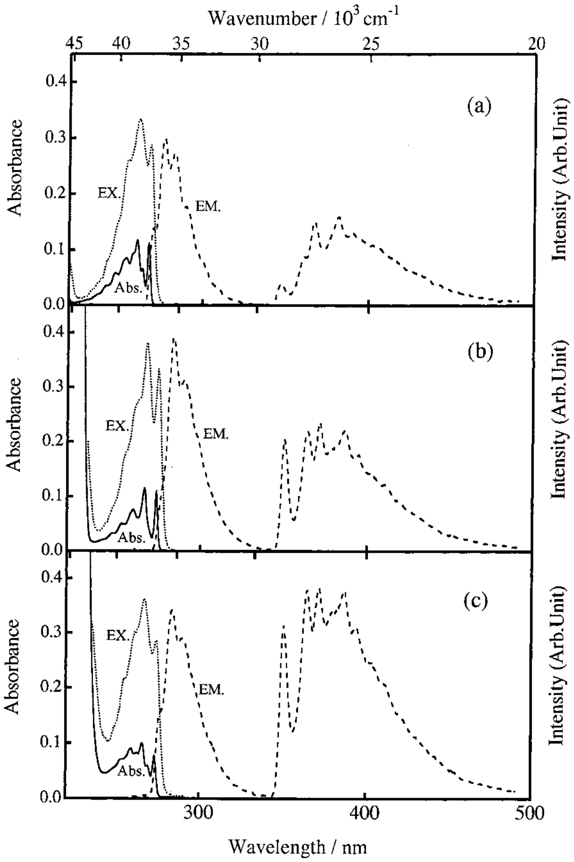


Figure 2. Electronic absorption spectra (full line) and emission (broken line) and excitation spectra (dotted line) of toluene (a), benzyltrimethylsilane (b), and trimethylsilyldiphenylmethane (c) in 3-methylpentane at 77 K.

former being smaller than the fluorescence quantum yield of **1** (0.31) at 77 K.[9] The fluorescence decay profile of **2** was determined by monitoring the emission at 300 nm upon excitation at 266 nm, and the fluorescence lifetime (τ_f) was determined to be 25 ± 2 ns in 3MP and 22 ± 2 ns in EtOH at 77 K by analyzing with a single-exponential function. Using these values, the radiative rate constant of fluorescence, k_f^0, and the nonradiative rate constant, k_{nr}, have been calculated by the following equations.

$$k_f^0 = \Phi_f/\tau_f \quad (1)$$

$$k_{nr} = (1/\Phi_f - 1)\, k_f^0 \quad (2)$$

Values of k_f^0 and k_{nr} of **2** were estimated to be 9.2 × $10^6\ s^{-1}$ and 3.1 × $10^7\ s^{-1}$ in 3MP and 9.1 × $10^6\ s^{-1}$ and 3.6 × $10^7\ s^{-1}$ in EtOH, respectively.

The phosphorescence quantum yields (Φ_p) of **1** and **2** in 3MP at 77 K were also experimentally determined, relative to that of toluene, to be 0.34 ± 0.05 and 0.39 ± 0.03, respectively. These values are comparable with Φ_p of toluene (0.26)[11] and diphenylmethane (0.41),[12] respectively. Phosphorescence decay profiles of **1** and **2** were measured by monitoring the emission at 380 nm upon excitation at 250 nm, and their phosphorescence lifetimes (τ_P) were determined to be 1.1 ± 0.1 s and 0.9 ± 0.1 s, respectively.

Photophysical parameters of **1** and **2** at room temperature were determined in the same way as those at 77 K. All photophysical parameters obtained for fluorescence are summarized in Table 1 in comparison with those of toluene. It is noted here that the fluorescence of **2** at room temperature is very weak and its lifetime was too short to be measured. Hence, the radiative rate constant (k_f^0) of **2** was estimated by use of the equation given by Strickler and Berg[13] as to be ca. 1 × $10^7 s^{-1}$. The nonradiative rate constant (k_{nr}) was then estimated to be ca. 2 × $10^9\ s^{-1}$, being greater by 2 orders of magnitude than that determined at 77 K. This great nonradiative rate constant is considered to be responsible for the weak fluorescence of **2** at room temperature. As shown in Figure 1c, the ^1L_a band of **2** is shifted to red at room temperature, and as a result, the interaction between the ^1L_b state and the ^1L_a state may become significant to bring about the fast nonradiative decay. According to the calculated results for **1** and **2** by the CNDO/S-CI method, ^1L_a states of **1** and **2** have predominant contribution from the HOMO−LUMO singly excited configuration with contribution weight of ca. 94%. These two MO's are of bonding and antibonding character (ca. 20%) with respect to the C(benzyl)-Si bond, and therefore, in the ^1L_a state, a considerable elongation of the C−Si bond can be expected, and as a result, this may give a low-lying deformed electronic state responsible for the fast decay process as is discussed in a previous paper.[9] It is noted that these MO's result from the interaction between π-orbitals on phenyl ring and C−Si σ-orbitals (pseudo-π-orbital), and are considered to be characteristic of benzylsilane compounds.

Steady-State Photolysis of Trimethylsilyldiphenylmethane at 77 K. Trimethylsilyldiphenylmethane (**2**) was photolyzed at 77 K by irradiation with 266-nm light. Figure 3 shows absorption spectra of **2** before (dotted line) and after (full line) the photolysis in EtOH (a) and in 3MP (b) at 77 K. An intense

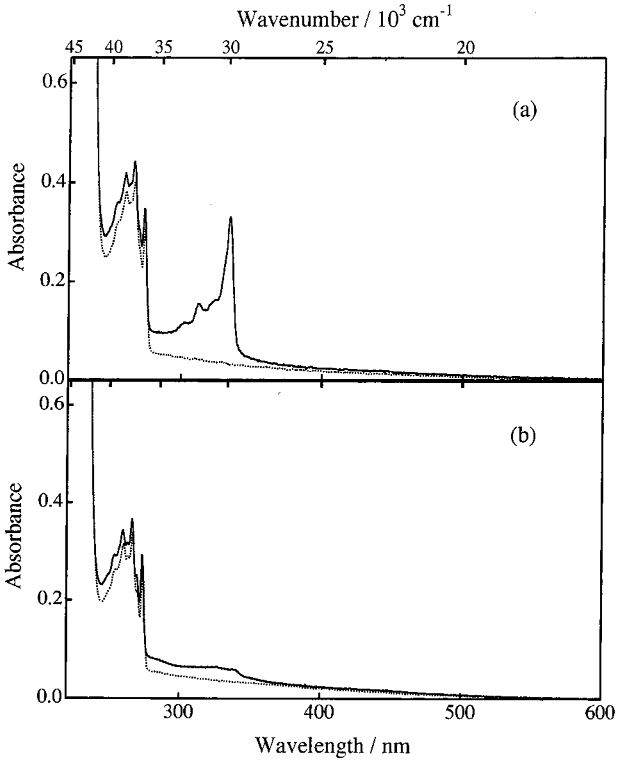


Figure 3. Absorption spectra of trimethylsilyldiphenylmethane before (dotted line) and after (full line) the photolysis in ethanol (a) and in 3-methylpentane (b) at 77 K.

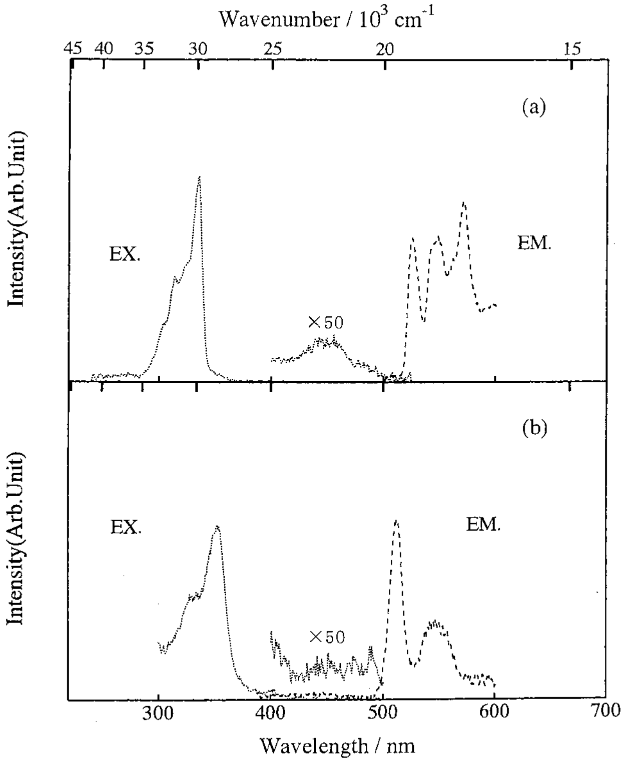


Figure 4. Fluorescence emission (broken line) and excitation spectra (dotted line) observed for trimethylsilyldiphenylmethane after the photolysis in ethanol (a) and in 3-methylpentane (b) at 77 K.

peak was observed at 335 nm in EtOH after the photolysis. This absorption band is very similar to those of diphenylmethyl radicals produced by UV photolysis or γ-radiolysis of diphenylmethyl chloride reported by Bromberg and Meisel[14] and Andrew et al.,[15] and therefore the 335-nm absorption band is ascribable to diphenylmethyl radicals.

When the 335-nm absorption peak was excited, the fluorescence emission spectrum was observed with peaks at 523, 555, and 570 nm as shown in Figure 4a (broken line). By monitoring the fluorescence at 570 nm, an excitation spectrum (dotted line) was observed with a peak at 335 nm in accord with the absorption spectrum. The fluorescence lifetime monitored at the 570-nm emission was determined to be 300 ns, which is comparable to that of diphenylmethyl radicals (330 ns).[16] The fluorescence emission and excitation spectra are also very similar to those of diphenylmethyl radicals produced from diphenylmethyl chloride.[14]

On the other hand, in 3MP the 335-nm absorption band due to diphenylmethyl radicals was not observed, but instead of it, a weak and broad absorption band appears in the region 300–360 nm as shown in Figure 3b. The broad absorption band disappeared when the temperature of the sample was elevated to room temperature and therefore is ascribable to unstable reaction intermediate(s). This kind of solvent effect on the photolysis was observed for benzyltrimethylsilane (**1**) as reported in a previous paper;[9] in the photolysis of **1** in EtOH glass, benzyl radicals were predominantly produced by nucleophilic reaction with alcohol, while in 3MP glass, the benzyl radical was not produced but the α-trimethylsilylbenzyl radical and the radical cation of **1** were formed biphotonically via the lowest triplet state. In the photolysis of **2** in 3MP glass, C–H bond scission is also expected to take place similar to the case of **1** to give α-trimethylsilyldiphenylmethyl radicals. Figure 4b shows fluorescence excitation and emission spectra observed after the photolysis of **2** in 3MP. Although the absorption spectrum of **2** photolyzed in 3MP did not show any intense peak around 335 nm, the excitation of the 335-nm absorption gave a fluorescence spectrum with peaks at 510 nm and around 545 nm, being similar to that of diphenylmethyl-type radicals produced from diphenylmethyl chloride by γ-radiolysis.[14] By monitoring the fluorescence at 510 nm, an excitation spectrum with an intense peak at 350 nm was observed. The fluorescence decay profile observed at 510 nm was measured by excitation at 350 nm. This decay was analyzed by a single exponential function, and its fluorescence lifetime was determined to be 390 ± 20 ns, being definitely longer than that of diphenylmethyl radicals at 77 K (300 ns). By taking into consideration the spectral characteristics and fluorescence lifetime, the weak fluorescence observed in 3MP is ascribable to α-trimethylsilyldiphenylmethyl radicals. The sharp band at 350 nm in the excitation spectrum corresponds to the longest wavelength absorption in the broad absorption band shown in Figure 3b. The predominant species responsible for the broad absorption is nonemissive and no further information was obtained, but as a candidate of this species the radical cation of **2** may be pointed out based on the results observed for **1**.[9] As a result, it is concluded that upon the photolysis in EtOH diphenylmethyl radicals were exclusively produced, while in 3MP a trace of α-trimethylsilyldiphenylmethyl radicals and unknown product(s) (possibly the radical cation) were formed.

Formation quantum yields of the benzyl radical and diphenylmethyl radical were determined for **1** and **2** in EtOH at 77 K by use of tris(oxalato)ferrate(III) as a chemical actinometer. By assuming the molar absorption coefficient of benzyl radical to be 8800 M^{-1} cm^{-1} at 318 nm[17] and that of the diphenylmethyl radical to be 44 000 M^{-1} cm^{-1} at 335 nm,[18] the quantum yields were estimated to be $6 \pm 2 \times 10^{-3}$ and $7 \pm 2 \times 10^{-3}$, respectively. These low quantum yields indicate that the reaction path to give benzyl-type radicals is not a major deactivation process of the excited state of **1** and **2** at 77 K.

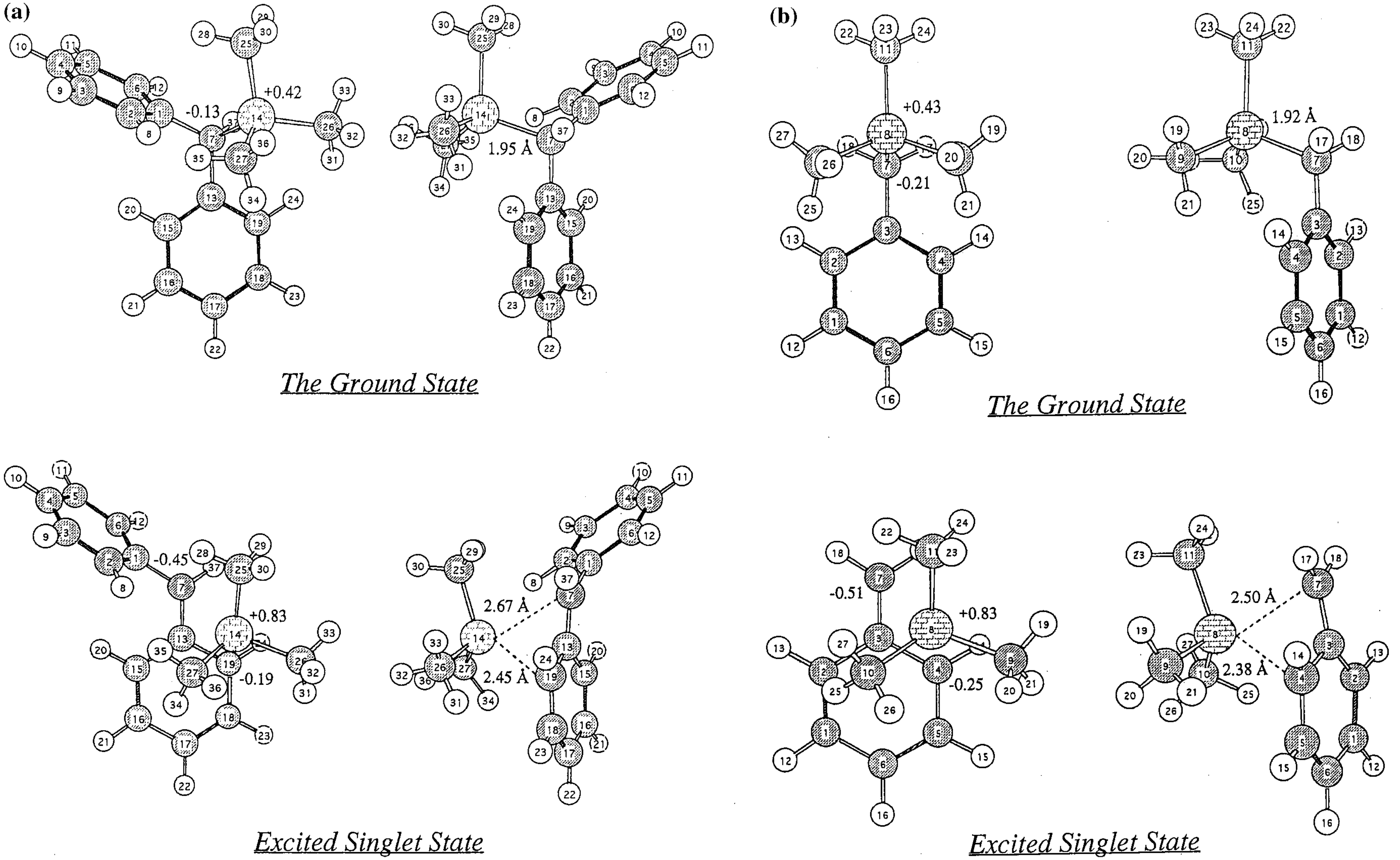
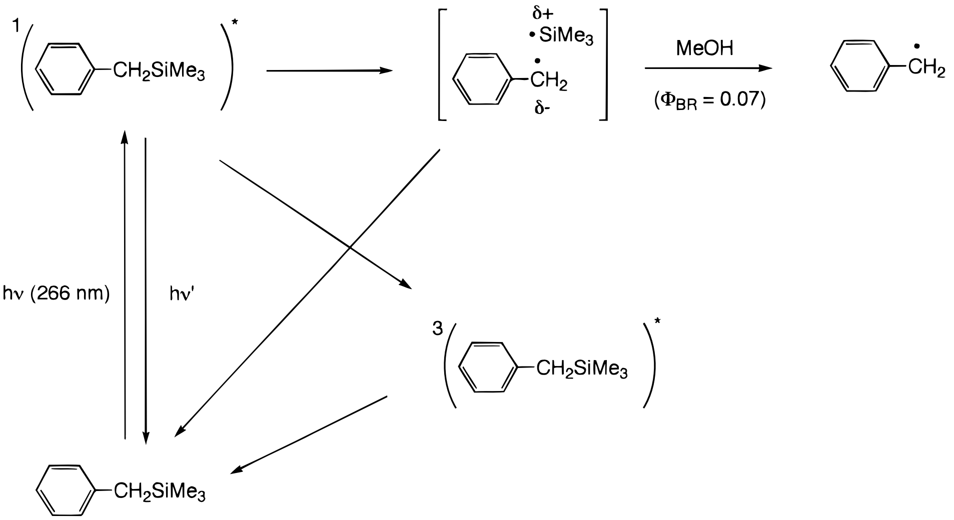


Figure 5. Molecular structures calculated for the ground state and excited singlet state of trimethylsilyldiphenylmethane (a) and benzyltrimethylsilane (b).

SCHEME 1: Primary Photochemical Processes of Benzyltrimethylsilane at Room Temperature



To examine whether the lowest triplet state is responsible for the formation of these reaction intermediates, a sufficient amount (more than 0.80 mol/L) of triplet quencher, 2,3-dimethyl-1,3-butadiene, whose triplet energy is 253 kJ mol^{-1},[19] was added to the solutions so that all the phosphorescence was essentially quenched. When these solutions were irradiated with 266 nm light, the broad absorption band in 3MP was not observed, but in EtOH the 335 nm band due to diphenylmethyl radicals was still observed. These results indicate that the diphenylmethyl radicals are produced via the excited singlet state or a higher triplet state, though the partial formation via the lowest triplet state is not still denied and α-trimethylsilyldiphenylmethyl radicals are predominantly produced via the lowest triplet state.

The remarkable solvent effect on the formation of reaction intermediates observed for **1** was explained by considering a unique excited state (denoted as X-state) calculated by the PM3 method.[9] It is noted that an ab initio calculation of **1** gives the excited singlet state with similar molecular structure to this.[20] As shown in Figure 5a, similar results were calculated for the excited singlet state generated by the HOMO−LUMO transition of **2** by PM3 calculations, which is originally of ^1L_a character.

Recalculated results for **1** are also shown in Figure 5b for comparison. Molecular structures of these excited states are remarkably deformed compared to that of the ground state. Definitely longer interatomic distance than a normal Si−C single bond (1.94 Å) was calculated for the Si−C bond (2.67 Å) between the silicon (14) and methylene carbon (7) atoms. The Si(14)−C(7) bond length is greater than those calculated for the Si−C bonds between Si(14) and *ortho*-carbon (19) (2.45 Å) and Si(14) and *ipso*-carbon atoms (2.36 Å). The atomic charges of the silicon, methylene, *ortho*-, and *ipso*-carbon atoms were calculated to be +0.83, −0.45, −0.19 and +0.08 for the excited state, respectively, and the bond orders of Si(14)−C(7) (0.09), Si(14)−C(19) (0.20), and Si(14)−C(13) (0.24) are much smaller than those of a normal Si−C single bond. As in the case of **1**, this calculated excited state is considered to be responsible for the nucleophilic reaction with alcohol to give diphenylmethyl radicals. It is noted that the fluorescing state is different from this deformed excited state because the structure of the fluorescing state is considered to be similar to that of the ground state based on the experimental results; a small Stokes shift and a good mirror-image relationship between the absorption and emission spectra as shown in Figure 2. In fact, the fluorescing state is assigned to the ^1L_b state, while the deformed excited singlet state is correlated with ^1L_a state generated by HOMO−LUMO transition. It is pointed out that this deformation may be responsible for the fast nonradiative decay process of **2** at room temperature. To study solvent effects on the formation of diphenylmethyl radicals, photolyses of **2** were carried out in MeOH, EtOH, 2-propanol (2-PrOH), 2-butanol (2-BuOH), and 1-butyronitrile (BuCN). The relative formation yields of diphenylmethyl radicals were estimated to be 2.1, 1.0, 0.6, and 0.0 for MeOH, EtOH, 2-PrOH, and 2-BuOH, respectively. This is in accord with the order of dielectric constant of these alcohols; 32.6 (MeOH), 24.6(EtOH), 19.9(2-PrOH), and 17.5 (2-BuOH). To examine whether the proton is responsible for this reaction or not, photolysis of **2** was carried out in a polar aprotic solvent, BuCN, whose dielectric constant is 20.3. The absorption spectrum observed for **2** after the photolysis in BuCN showed a characteristic peak at 335 nm due to diphenylmethyl radicals. Thus, BuCN is a more effective nucleophile than BuOH, though both are sterically unfavorable for the nucleophilic reaction. The results indicate that the reactivity of **2** with alcohols is not related to proton donating ability but to charge density on the oxygen atom.

Laser Flash Photolysis of Benzylsilanes at Room Temperature. Figure 6 shows the transient absorption spectra of **1** in MeOH (a) and cyclohexane (CH) (b) determined at 3, 4, 5, 10, 20, 50, and 180 μs after the laser flash at room temperature. For both spectra, a broad absorption band was observed in the region of 300−450 nm, and in addition to this broad band a moderately intense band was observed with a peak at 316 nm in MeOH as shown in Figure 6a. The broad absorption band disappeared in the presence of oxygen and therefore is ascribable to T−T absorption. The decay profiles monitored at 316 and 380 nm are shown in insets of parts a and b of Figure 6, respectively. The decay profile at 380 nm was not analyzed by a single-exponential decay function but was analyzed by a combination of first- and second-order decay, the latter being due to T−T annihilation. Best-fitting curves were obtained with decay rate constants of $k_1 = 1.6 \times 10^5$ s^{-1} and $k_2 = 2.0 \times 10^7 \epsilon_{T-T}$ M^{-1} s^{-1} for the unimolecular decay and T−T annihilation in MeOH, respectively, and also with $k_1 = 1.6 \times 10^5$ s^{-1} and $k_2 = 3.8 \times 10^6 \epsilon_{T-T}$ M^{-1} s^{-1} in CH, respectively.

Claridge and Fischer reported that benzyl radicals show a characteristic absorption band at 316 nm in CH at room temperature,[17] and therefore the 316-nm transient absorption is considered to be composed of two absorptions due to the benzyl radical and the triplet. The decay time profile at 316 nm was

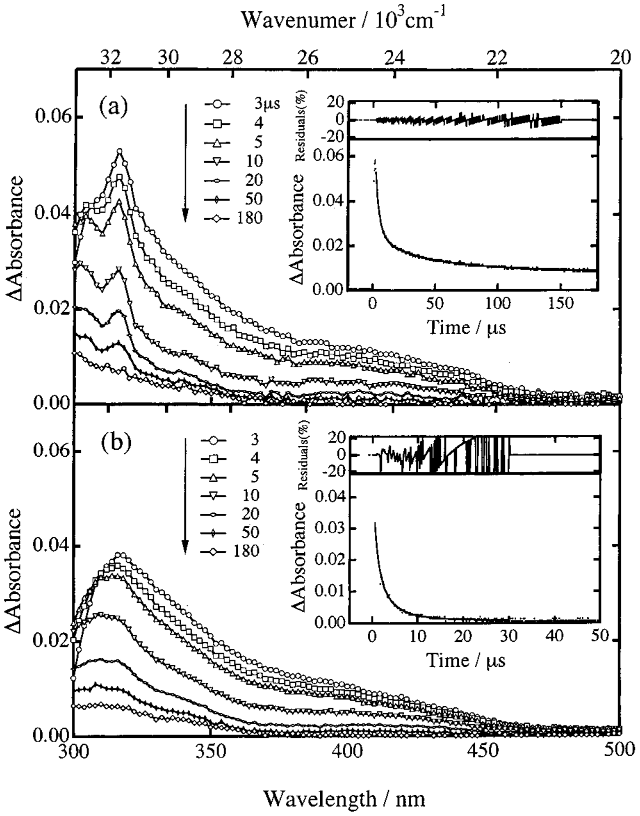


Figure 6. Transient absorption spectra observed upon the 266-nm light photolysis of benzyltrimethylsilane in methanol (a) and in cyclohexane (b) saturated with Ar at room temperature. Decay profiles monitored at 316 and 380 nm are shown in the insets of (a) and (b), respectively.

TABLE 2: Decay Rate Constants of Transient Species Produced by the 266-nm Light Photolysis of Benzyltrimethylsilane at Room Temperature[a]

	benzyl radical			triplet	
solvent	$2k_2$ [M^{-1} s^{-1}]	k_{diff} [M^{-1} s^{-1}]	$2k_2$ [M^{-1} s^{-1}][b]	k_1' [s^{-1}]	k_2' [M^{-1} s^{-1}]
CH		7.4×10^9	4.6×10^9	1.6×10^5	$3.8 \times 10^6 \epsilon_{\mathrm{T-T}}$[c]
MeOH	1.1×10^{10}	1.2×10^{10}		1.6×10^5	$2.0 \times 10^7 \epsilon_{\mathrm{T-T}}$

[a] Error, ±15%. [b] Reference 17. [c] $\epsilon_{\mathrm{T-T}}$, molar absorption coefficient of T−T absorption.

analyzed by the sum of a combination of first- and second-order decay for the T−T absorption and a second-order decay for benzyl radicals. By keeping the decay rate constant of the T−T absorption at the same value determined for the decay of triplet at 380 nm, the best-fitted curve shown in the inset of Figure 6a (full line) was obtained with a second-order rate constant of $2k_2 = 1.1 \times 10^{10}$ M^{-1} s^{-1} for benzyl radicals, where the molar absorption coefficient of the benzyl radical was assumed to be 8800 M^{-1} cm^{-1} at 316 nm. This value is slightly smaller than the diffusion rate of MeOH (1.2×10^{10} M^{-1} s^{-1}) and is greater than the decay rate constant $2k_2$ (4.6×10^9 M^{-1} s^{-1}) determined by the modulation transient spectroscopy of benzyl radicals produced from dibenzyl ketone in cyclohexane,[17] whose diffusion rate is 7.4×10^9 M^{-1} s^{-1}. These decay rate constants are summarized in Table 2.

Thus, upon the laser flash photolysis of **1** in MeOH, the triplet and benzyl radicals were produced, while in CH only a broad absorption band ascribable to T−T absorption was observed. This difference can be explained by the reactivity of **1** in the excited singlet state with MeOH. These results are consistent with those of the photolysis at 77 K,[9] where benzyl radicals were predominantly produced in EtOH by nucleophilic reaction in the excited singlet state (or a higher triplet state) and α-trimethylsilylbenzyl radicals were produced by a biphotonic process in nonpolar 3MP via the T_1 state. These results are summarized in Scheme 1.

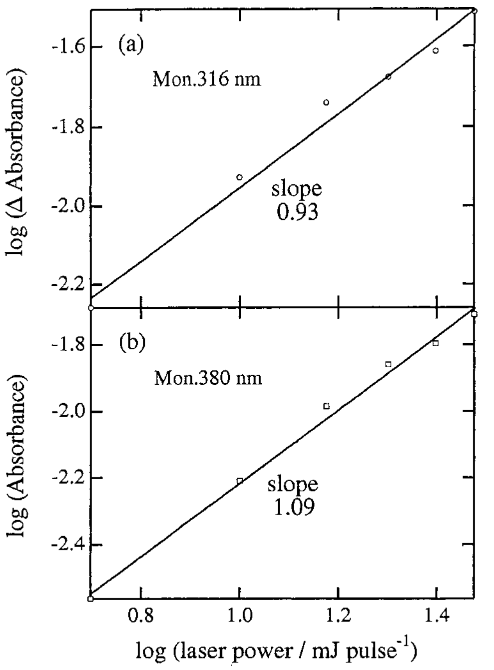


Figure 7. Laser power dependence of transient absorptions monitored at 316 nm (a) and 380 nm (b) in methanol at 1 μs after the laser pusling.

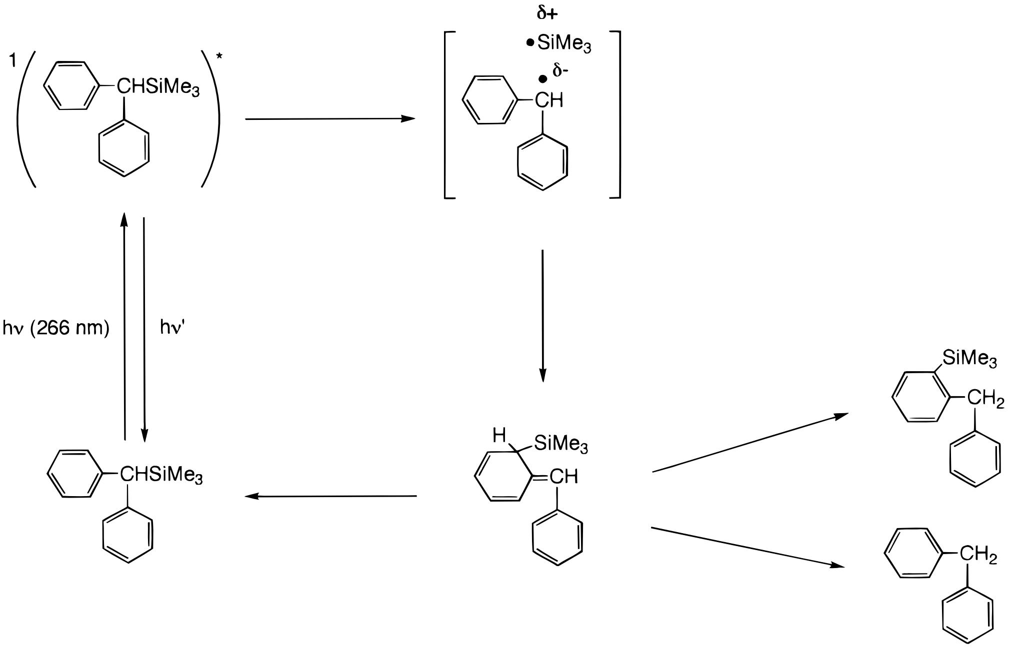
Dependence of benzyl radical formation against the excitation laser power was examined by monitoring the transient absorption at 316 nm in MeOH, and the result is shown in Figure 7a along with that of T−T absorption at 380 nm shown in Figure 7b. Straight lines with the slope of ca. 1.0 were obtained for both plots, indicating that formation of both the benzyl radical and triplet are monophotonic. Recently, Fujiwara and Tanimoto studied the formation process of *ortho*-methylbenzyl radicals from *ortho*-xylene at room temperature by use of a two-pulse laser-induced fluorescence technique and reported that the formation of *ortho*-methylbenzyl radicals is monophotonic and formed from the thermally equilibrated S_1 state by predissociation.[21] On the other hand, Koyanagi and Uejoh reported that the formation process of the benzyl radical from toluene at 77 or 4.2 K is unimolecular and biphotonic.[22] Biphotonic formation of α-trimethylsilyldiphenylmethyl radicals at 77 K is consistent with their results, but formation of benzyl radicals in the photolysis of **1** is different from the case of xylene, because in nonpolar solvent absorption band attributable to benzyl radicals was not observed. This difference may be due to the difference in electronic structure brought by the interaction of the π-electron system with the C−Si σ-bond.

Quantum yield of the benzyl radical (Φ_{BR}) generated upon the laser photolysis of **1** was determined at room temperature by estimating the concentration of benzyl radicals, [BR], and number of photons, I_{abs}, absorbed by **1** at 266 nm. [BR] was estimated by the equation

$$[\mathrm{BR}] = A_{\mathrm{BR}}/\epsilon_{\mathrm{BR}} \qquad (3)$$

where A_{BR} was determined from the absorbance at 316 nm and ϵ_{BR} is the molar absorption coefficient of the benzyl radical at 316 nm (8800 M^{-1} cm^{-1}).[17] I_{abs} was determined by using naphthalene as a chemical actinometer of which quantum yield

SCHEME 2: Primary Photochemical Processes of Trimethylsilyldiphenylmethane at Room Temperature



of intersystem crossing to the lowest triplet state (Φ_T) is 0.8 and by using the molar absorption coefficient of T−T absorption at 415 nm (ϵ_{T-T} = 24 500 M^{-1} cm^{-1}).

$$I_{abs} = (A_{NP}/\epsilon_{T-T})x(1/\Phi_T)N_A \qquad (4)$$

where A_{NP} and N_A are the transient absorption of naphthalene observed at 415 nm under the same experimental conditions and Avogadro number, respectively. Using these values, Φ_{BR} is calculated by the equation

$$\Phi_{BR} = [BR]/(I_{abs}/N_A) \qquad (5)$$

Plot of [BR] against I_{abs}/N_A gave a straight line with a slope of ca. 0.07; Φ_{BR} = 0.07 in MeOH. This result indicates that benzyl radicals are generated rather efficiently at room temperature upon excitation compared with the photolysis at 77 K (ca. 6×10^{-3}) where molecular motion is significantly suppressed.

Parts a and c of Figure 8 show the transient absorption spectra of **2** in MeOH and CH, respectively, determined at 0.5, 1, 10, and 45 μs after the laser pulsing. In both solvents, a broad absorption band was observed in the region of 280−450 nm, but the absorption band ascribable to diphenylmethyl radicals was not observed even in MeOH. These broad bands did not decay in the microsecond time scale range. They were not quenched by oxygen and therefore are not ascribable to T−T absorption, in contrast to the case of **1**. Parts b and d of Figure 8 show the transient absorption spectra of **2** in MeOH and CH, respectively, determined at 1, 10, 20, 40, and 90 ms after the laser pulsing. The decay profiles observed at 350 nm in MeOH and in CH were analyzed by first-order kinetics, and the best-fitted curves were obtained with decay rate constants of 25 and 29 s^{-1}, respectively. Decay rate constants of the broad band in the presence of oxygen were also determined to be 26 and 28 s^{-1} in MeOH and in CH, respectively, and no effect of oxygen on the decay was observed even in this time scale. These decay rates constants are summarized in Table 3 in comparison with those of photo-Fries rearranged isomers.

Laser power dependence of the formation of the long-lived transient species was studied by examining the log−log plot of the transient absorption at 350 nm against laser power. A straight line was obtained, and the slope was ca. 1.0, indicating that the formation process is monophotonic. As a result, it is understood

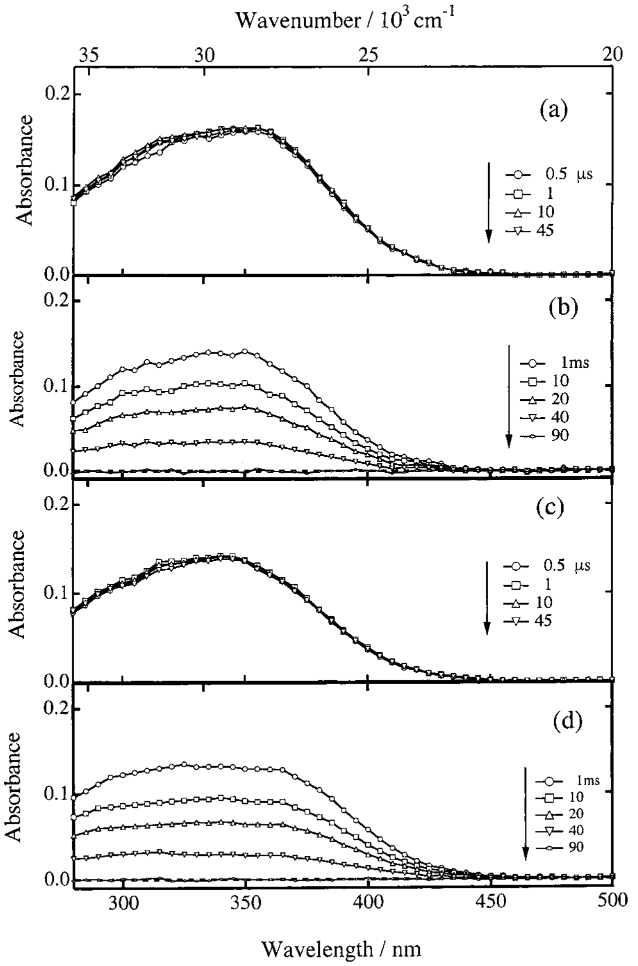


Figure 8. Transient absorption spectra in the microsecond and millisecond time scale observed upon the 266-nm light photolysis of trimethylsilyldiphenylmehthane in methanol, (a) and (b), and in cyclohexane, (c) and (d), respectively, saturated with Ar at room temperature.

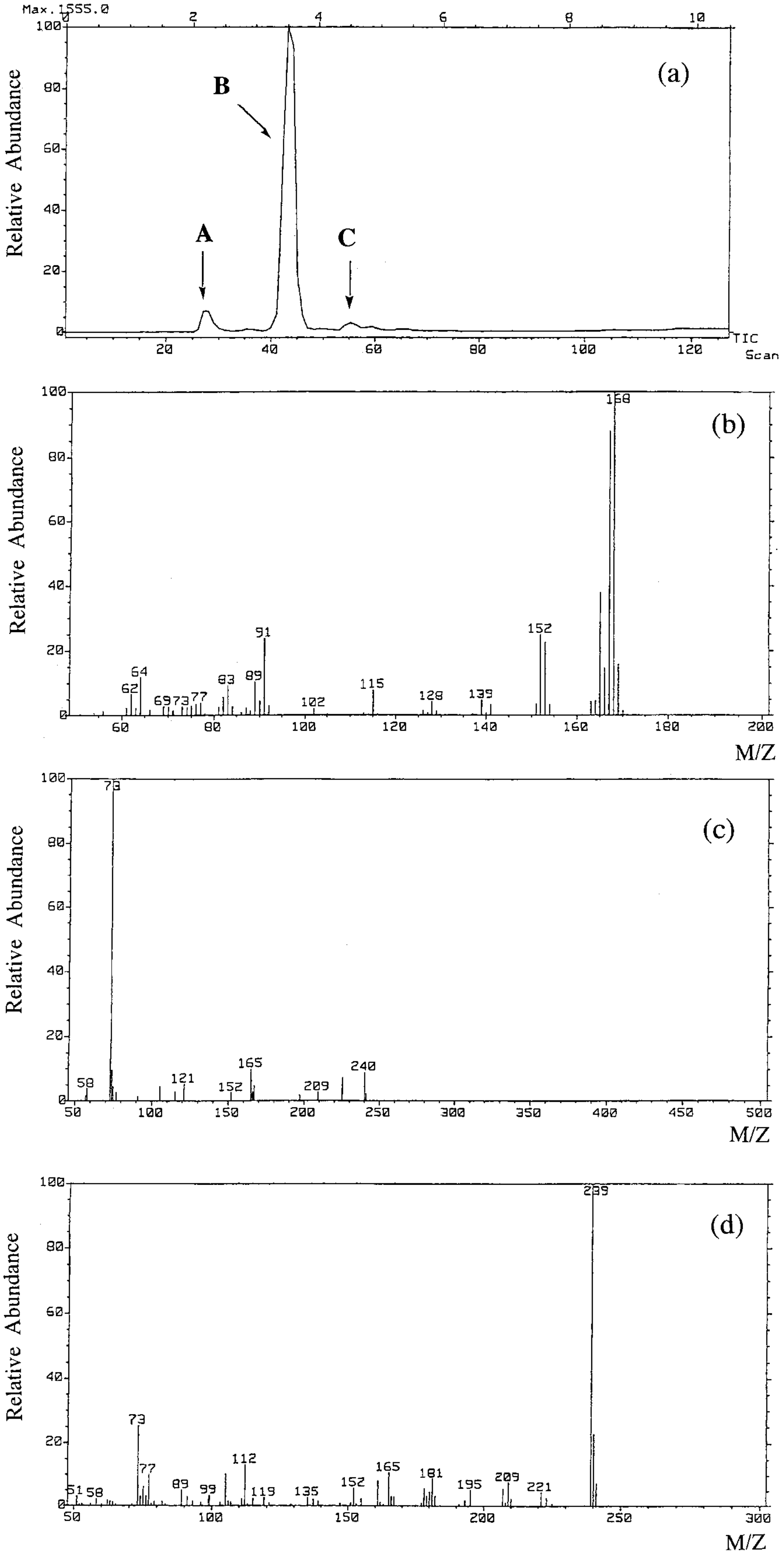


Figure 9. GC-MS spectra obtained for the photoproducts of trimethylsilyldiphenylmethane after the 266-nm photolysis. MS spectra obtained for three peaks denoted as A, B, and C in the GC chart (a) are shown in (b), (c), and (d), respectively.

that the long-lived species are formed via the excited singlet state (or a higher triplet state). Such characteristic long lifetime and insensitivity to oxygen were observed for the ortho-rearranged intermediates generated in the photolysis of phenylacetate.[24] The ortho-rearranged intermediates of phenylacetate show a broad absorption band around 300 nm which decays with a rate constant of 50 s^{-1} in acetonitrile. Furthermore, the ortho-rearranged intermediates of phenylacetate are not quenched

TABLE 3: Decay Rate Constants of Transient Species Produced by the 266-nm Light Photolysis of Trimethylsilyldiphenylmethane at Room Temperature[a]

	o-rearranged intermediates [s^{-1}]		photo-Fries rearranged intermediates [s^{-1}][b]	
solvent	Ar bubbling	O_2 bubbling	1,3-shift	1,5-shift
CH	29	28	3.6	6.5×10^{-2}
MeOH	25	26	3.0×10^{5}	2.5×10^{5}

[a] Error, ±10%. [b] Reference 24.

by oxygen and decay unimolecularly to give *ortho*-hydroxyacetophenone.[24] According to the resemblance in the lifetime and spectral shape of absorption band the broad transient absorption band is attributable to the 1,3-silyl-shifted isomer of **2**.

To examine the formation of the rearranged isomer, product analysis was carried out by measuring the GC-MS of the photoproducts obtained by irradiation with 266-nm light in MeOH at room temperature. Three peaks denoted as A, B, and C were observed in the GC chart as shown in Figure 9a with relative intensities of 6.5%, 91%, and 2.5%, respectively. The MS spectrum of the most intense peak, B, shown in Figure 9c is essentially the same as that of parent molecule **2.** The MS spectrum of peak A (Figure 9b) gave typical fragmentation peaks at 168 *m*/*z* (molecular ion), 167 (molecular ion − 1), and 91 (benzyl ion) and is essentially the same as the MS spectrum of diphenylmethane. Therefore, peak A is ascribable to diphenylmethane produced from **2** by losing a trimethylsilyl group. In the MS spectrum of peak C shown in Figure 9d, the most prominent peak is observed at 239 *m*/*z* which is ascribable to the molecular ion − 1. Also, a trimethylsilyl ion is observed at 73 *m*/*z* and, in addition, moderately intense signals at 165 and 152 *m*/*z* commonly observed for A and B are observed for C. These results indicate that the peak **C** is ascribable to the species having a diphenylmethyl skeleton and a trimethylsilyl group. Thus, peak C is ascribable to the rearranged isomer of trimethylsilyldiphenylmethane. These results are consistent with our assignment of the broad absorption band to ortho-rearranged intermediates. The *ortho*-trimethylsilyldiphenylmethane which is considered to be responsible for the peak C can be formed when a 1,3-hydrogen shift takes place in ortho-rearranged intermediates. Ortho-rearranged intermediates, however, may preferentially undergo a reverse 1,3-silyl group shift to form parent molecule, **2**, as suggested by a relatively weak peak of **C**.

The calculated molecular structure of the excited singlet state generated by HOMO−LUMO transition of **2** shown in Figure 5a also suggests the possibility of the formation of the 1,3-silyl-shifted isomer, where the bond order of Si−C (ortho) is greater than that of Si−C (methylene) in the deformed excited state. Thus, upon the laser flash photolysis of **2** at room temperature, ortho-rearranged intermediates are considered to be predominantly formed via the deformed excited singlet state in both MeOH and CH, different from the low-temperature photolysis. 1,3-Silyl group shifts similar to this case were also observed for the photolyses of pentamethyldisilane[26−29] and methylpentaphenyldisilane.[30]

It is interesting that the photochemical reaction of **2** at room temperature is different from that at 77 K**.** This difference may partially be ascribed to the difference in stability of the 1,3-silyl-shifted intermediates at these temperatures. Activation energy from the deformed excited state to the ortho-rearranged isomer of **2** may be also responsible for this difference. The activation energy is considered to be small because the latter was produced even in the photolysis at 130 K. The reaction mechanism of **2** at room temperature is summarized in Scheme 2.

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