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# Laser Pulse Photolysis of 7-Silanorbornadiene in Solution: Experimental and AM1 Studies of Complexation between Silylenes and $\text{CHBr}_3$

Marc B. Taraban,\* Victor F. Plyusnin, Olga S. Volkova, Vyacheslav P. Grivin, and Tatyana V. Leshina

*Institute of Chemical Kinetics and Combustion, Institutskaya str. 3, Novosibirsk-90, 630090 Russia*

Vladimir Ya. Lee, Valery I. Faustov, Mikhail P. Egorov,\* and Oleg M. Nefedov

*N. D. Zelinsky Institute of Organic Chemistry, Leninsky prosp. 47, Moscow, 117913 Russia*

*Received: February 13, 1995; In Final Form: June 15, 1995*

The quantum yield ( $0.95 \pm 0.1$ ) for the decomposition of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**Ib**) in hexane at room temperature has been determined by the laser pulse photolysis technique. Reaction rate constants of the generated dimethylsilylene with bromoform ( $4.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) and **Ib** ( $5.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) have been measured. It is suggested that the reaction of  $\text{Me}_2\text{Si}:$  with  $\text{CHBr}_3$  occurs via the formation of an intermediate complex ( $\lambda_{\text{max}} = 338 \text{ nm}$ ,  $\epsilon = 1280 \text{ M}^{-1} \text{ cm}^{-1}$ ). The bimolecular rate constant for decay of the complex ( $2k = 1.61 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) has also been estimated. Semi-empirical PM3 calculations of the model reaction between singlet  $\text{SiH}_2$  and  $\text{CHBr}_3$  show the formation at the first step of the reaction of a donor–acceptor complex stabilized by interactions between a vacant p-AO of  $\text{SiH}_2$  and a lone electron pair of one of the Br atoms. Such a complex should be rather stable both toward dissociation into the starting reagents ( $E = 23.3 \text{ kcal/mol}$ ) and further rearrangement into the insertion product,  $\text{Br}(\text{H}_2)\text{-SiCHBr}_2$  ( $E = 22.3 \text{ kcal/mol}$ ).

## Introduction

Silylenes and germylenes constitute an important class of reactive intermediates from both theoretical and synthetic points of view.<sup>1–3</sup> However, a restricted number of convenient precursors of silylenes and germylenes is known; therefore 7-sila- and 7-germanorbornadienes are of special significance among them.<sup>2,3</sup> These compounds generate  $\text{R}_2\text{E}$  ( $\text{E} = \text{Si}, \text{Ge}$ ) species upon photolysis or thermolysis. The mechanisms of photochemical and thermal decomposition of the derivatives of 7-sila(germa)norbornadienes **I** ( $\text{E} = \text{Si}, \text{Ge}$ ) have been studied using the  $^1\text{H}$  CIDNP technique.<sup>4–6</sup>

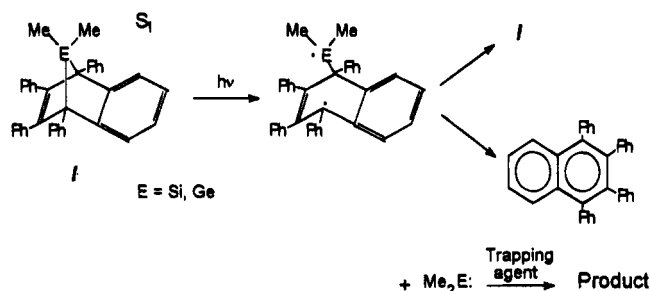
The analysis of nuclear polarization effects observed both in the presence and in the absence of various trapping agents of  $\text{Me}_2\text{Si}$  and  $\text{Me}_2\text{Ge}$  has allowed us to propose the scheme of photochemical decomposition, where the biradical species are assumed to be the precursors of corresponding silylenes and germylenes (Scheme 1).<sup>4,5</sup>

The formation of such a biradical has also been suggested to explain the results of photolysis of 7-germanorbornadiene in a matrix at 77 K.<sup>7</sup>

7-Germanorbornadiene (**Ia**) ( $\text{E} = \text{Ge}$ ) was one of the first among germylene precursors studied by the pulse photolysis technique.<sup>8</sup> The transient absorption at 380 nm arising after a light pulse was assigned to  $\text{Me}_2\text{Ge}$  (or, more probably, to a complex between  $\text{Me}_2\text{Ge}$  and 1,2,3,4-tetraphenylnaphthalene (TPN)).<sup>7,8</sup> 7-Silanorbornadiene (**Ib**) ( $\text{E} = \text{Si}$ ) has also been studied by laser pulse photolysis.<sup>9</sup> However, the results have caused some controversy concerning the detection of  $\text{Me}_2\text{Si}:$  in these experiments.

The present paper is devoted to laser pulse photolysis studies of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**Ib**) in the liquid phase, including experiments in the presence of  $\text{CHBr}_3$ . The main goal of the work is not only to

## SCHEME I



clarify the above mentioned obscurity but also, first of all, to obtain quantitative information on the elementary stages of photolysis and to compare these results with  $^1\text{H}$  CIDNP data. Semi-empirical PM3 calculations are used to explain some of the experimental results.

## Experimental Section

7,7-Dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene was synthesized according to the known procedure.<sup>10</sup>

The laser pulse photolysis setup with an XeCl excimer laser ( $\lambda = 308 \text{ nm}$ , pulse duration 15 ns, pulse energy 10 mJ) has been described earlier.<sup>11,12</sup> Measurements were performed in 1–2 mm quartz optical cells, with typical concentrations of **Ib** in laser pulse photolysis experiments being ca.  $10^{-3} \text{ M}$ . The angle between excitation and probing light beams was about  $2^\circ$ . Cells were mounted in a quartz optical cryostat for a wide range temperature variation. In the majority of kinetic experiments the wavelength of the probe light was equal to the wavelength where maximum absorption of the transient species has been detected,  $\lambda = 338 \text{ nm}$ . A 50 ns delay time was used for all transient spectra. Prior to experiments all solutions were deaerated either by 30 min of argon bubbling or by means of standard freeze–pump–thaw cycles. Optical spectra during the

\* Abstract published in *Advance ACS Abstracts*, September 15, 1995.

stationary photolysis were detected with a Specord UV-vis spectrophotometer (Karl Zeiss). All solvents for sample preparation were of UV-grade purity and were dried prior to use. Typical concentrations of **Ib** and 1,2,3,4-tetraphenylnaphthalene in stationary photolysis experiments were about  $10^{-4}$  M.

$^1\text{H}$  NMR spectra were recorded with a JEOL JNM FX90Q spectrometer (operating frequency 90 MHz for protons) equipped with a photochemical device for irradiation directly in the probe of the instrument.

GC/MS analysis was carried out on a Finnigan MAT INCOS 50 instrument, using RSL-200 columns (30 m  $\times$  0.25 mm, 50  $^\circ\text{C}$ ).

The following products of the photodecomposition of **Ib** were observed from GC/MS analysis and  $^1\text{H}$  NMR,  $\delta$  (ppm) from TMS given in parentheses:  $\text{Me}_2\text{Si}$  groups of **Ib** (0.04, 0.61);  $\text{Me}_2\text{SiBr}_2$  (1.02);  $\text{CH}_2\text{Br}_2$  (4.80);  $\text{CHBr}_2\text{--CHBr}_2$  (5.20); TPN (7.12).

Semi-empirical quantum chemical calculations were carried out using the PM3 method<sup>13</sup> as it was implemented in the MOPAC (Version 6)<sup>14</sup> package of programs. The geometries of molecules, intermediates, and transition states studied were calculated with full optimization. The nature of all the stationary points was verified by vibrational frequency calculations.

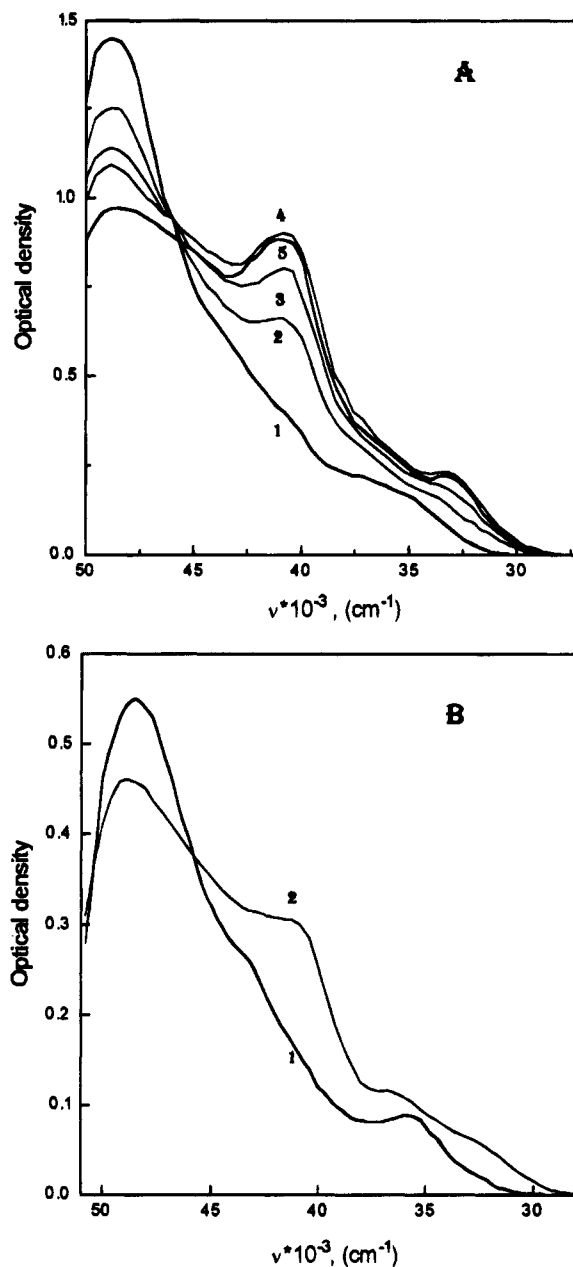
## Results and Discussion

Figure 1A shows the results of stationary photolysis of 7-silanorbornadiene (**Ib**) solutions in hexane (and/or methanol) at room temperature. These optical spectra clearly demonstrate that 1,2,3,4-tetraphenylnaphthalene (TPN),  $\lambda_{\text{max}} \approx 247$  nm is the sole reaction product with the light absorption in the spectral region from 330 to 500 nm. In spite of the fact that photolysis of **Ib** in methanol, in contrast to hexane, may lead to the products of  $\text{Me}_2\text{Si}$  insertion into the O-H bond of an alcohol molecule,<sup>1,15</sup> resulting UV spectra of the reaction mixture after irradiation in both hexane and methanol are nearly identical and show the formation of TPN only. The lack of the absorptions of other possible products could be due to low extinction coefficients of silicon-containing products in the UV region as compared to those of **Ib** and TPN ( $\epsilon \geq 5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). The second reason is the possibility of  $\text{Me}_2\text{Si(OMe)H}$  interference with TPN absorption in the far UV region.

Photolysis of **Ib** in a frozen methanol matrix at liquid nitrogen temperature (77 K) results in the appearance of an optical spectrum completely coinciding with that of tetraphenylnaphthalene under these conditions (Figure 1B). New absorption bands that could not be attributed to the signals of initial **Ib** or TPN are not detected. Note that the changes of the optical spectrum of **Ib** during irradiation in a frozen matrix are practically identical to the transformations of the spectrum of **Ib** in the photolysis in a liquid solution (Figure 1A).

The methanol matrix is considered to be one of the most rigid at 77 K; therefore, one could hardly expect the disappearance of dimethylsilylene in any reaction. From our viewpoint, the absence of additional absorption bands means that  $\text{Me}_2\text{Si}$  does not absorb the light of the visible region ( $\lambda > 350$  nm). Moreover, even if it has certain absorptions in the UV region, the extinction coefficients are considerably smaller than those of **Ib** and TPN (cf. ref 16).

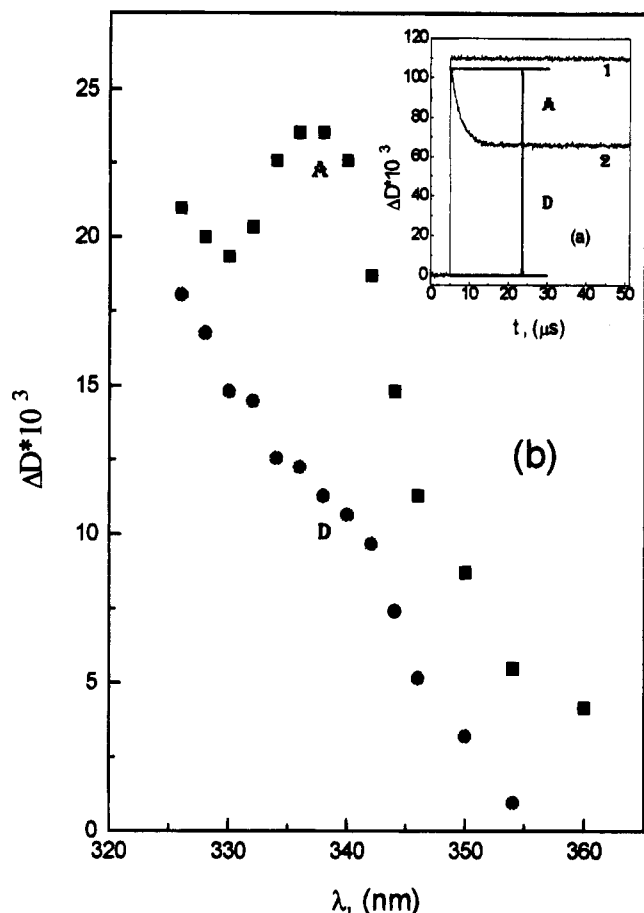
Addition of bromoform results in negligible changes of the absorption pattern of the photolysis of **Ib** in a matrix. Formation of TPN is not accompanied by the appearance of new absorption signals. It is also impossible to perform the analysis in the wavelength region with  $\lambda < 300$  nm because of the intense absorption of  $\text{CHBr}_3$ . However, the generation of a complex



**Figure 1.** (A) Variations of the UV-absorption spectrum of 7-silanorbornadiene (**Ib**) solution ( $2 \times 10^{-4}$  M) in hexane during stationary irradiation by nonfiltered light of a high-pressure mercury lamp DRSh-500 (500 W) at 295 K in a 1 mm cell. Irradiation time: (1–4) 0, 5, 10, and 20 s, respectively; (5) UV-absorption spectrum of tetraphenylnaphthalene (TPN) ( $2 \times 10^{-4}$  M in hexane). (B) Variations of the UV-absorption spectrum of 7-silanorbornadiene (**Ib**) solution ( $5 \times 10^{-4}$  M) in methanol (10% water) during stationary irradiation by nonfiltered light of a high-pressure mercury lamp DRSh-500 (500 W) at 77 K in a 0.2 mm cell. Irradiation time: (1, 2) 0 and 1 min, respectively.

between  $\text{Me}_2\text{Si}$  and  $\text{CHBr}_3$  in a matrix at 77 K is doubtful, since the mobility of partners under these conditions is completely suppressed. Annealing of a matrix to "thaw" the mobility does not lead to any definite result, as the presence of bromoform strongly worsens optical properties of the matrix at heating: it starts to scatter the light, becomes turbid, and loses optical transparency.

In laser pulse photolysis experiments with solutions of **Ib** in hexane without trapping agents, the sole absorption detected after the laser pulse in the region 330–500 nm was also associated with TPN only. The characteristic time of the appearance of this absorption is less than 50 ns, and after that it is stable within the experimental time scale (Figure 2a (1)).



**Figure 2.** Optical spectrum and the kinetics of formation and decay of the transient absorption during laser pulse photolysis of 7-silanorbornadiene (**Ib**) solutions,  $10^{-3}$  M in hexane ( $T = 296$  K,  $l = 1.17$  mm). Inset: (a) (1, 2) kinetic traces for the solutions with bromoform concentrations 0 and 0.1 M, respectively. (b) Optical spectra for signals A and D for the solution with bromoform concentration equal to 0.5 M. (See detailed description of the meaning of A and D in the main text.)

After several dozens of laser pulses, resulting in the formation of noticeable amounts of TPN, these molecules absorb part of the laser quanta. This leads to the appearance of a wide-band transient absorption with  $\lambda_{\max} \approx 450$  nm. Special experiments with TPN itself have shown that this is indeed the T–T absorption of TPN rather than the UV spectrum of dimethylsilylene. One should note that the transient absorption at  $\lambda_{\max} \approx 450$  nm has been ascribed to  $\text{Me}_2\text{Si}$  generated from other precursors in solutions.<sup>17</sup> The lifetime of the T–T absorption in deaerated solutions of TPN equals  $3 \mu\text{s}$ . It is quenched by oxygen with the reaction rate constant  $k_q = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . These data are in full agreement with the corresponding reference data on phenyl-substituted naphthalenes.<sup>18</sup>

Thus, we have not managed to detect the formation of  $\text{Me}_2\text{Si}$  in laser pulse photolysis of **Ib**. Evidently, this could be explained by an extremely short lifetime of the species in this particular case due to fast reaction with the precursor (see below). It is necessary to note that the transient absorption spectra of silylenes have been observed in laser pulse photolysis experiments, when other precursors that are considerably less reactive toward silylenes have been used.<sup>17</sup>

Note that the generation of dimethylsilylene in the photolysis of **Ib** in hydrocarbons is unambiguous, since we have earlier studied this reaction by the  $^1\text{H}$  CIDNP method.<sup>4</sup> The  $^1\text{H}$  CIDNP has also been employed to study the reaction of  $\text{Me}_2\text{Si}$  and  $\text{Me}_2\text{Ge}$  with halogenated radical traps (benzyl chloride and chlorotrimethylstannane).<sup>4</sup> The method has allowed detection of

radical pairs resulting from the abstraction of a halogen atom of a trap by  $\text{Me}_2\text{Si}$  or  $\text{Me}_2\text{Ge}$ . In this case, the formation of the products of heavy carbene insertion into the C–halogen bond of a trap has been observed (cf. reference data<sup>28</sup>). However, only the initial **Ib** and TPN are polarized in  $^1\text{H}$  CIDNP spectra when bromoform is used as a radical trap in the photolysis of **Ib** in cyclohexane and benzene. This observation points to the formation of  $\text{Me}_2\text{Si}$  (see Scheme 1). Other reaction products ( $\text{Me}_2\text{SiBr}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{CHBr}_2$ —see Experimental Section) do not demonstrate nuclear polarization. Our model calculations of the intensities of CIDNP effects formed in the radical pair resulting from the abstraction of the  $\text{CHBr}_3$  bromine atom by singlet  $\text{Me}_2\text{Si}$  have shown that the enhancement coefficients of the polarization are rather low ( $\approx 100$ ). The calculations have been performed using analytical expressions of the radical pair theory.<sup>29</sup> On the other hand, it is known that heavy carbene analogs  $\text{Me}_2\text{E}$  ( $\text{E} = \text{Si}, \text{Ge}$ ) form complexes with Lewis bases.<sup>1–3,15,19,28,30</sup> The complexation results in both an increase of the lifetime and a decrease of the reactivity of the complexes. These experimental observations do not explain, however, the absence of CIDNP effects, but nevertheless, one might expect that in the presence of  $\text{CHBr}_3$ , a molecule possessing atoms with lone electron pairs, the lifetime of the transient species will be long enough to allow their detection by laser pulse photolysis.

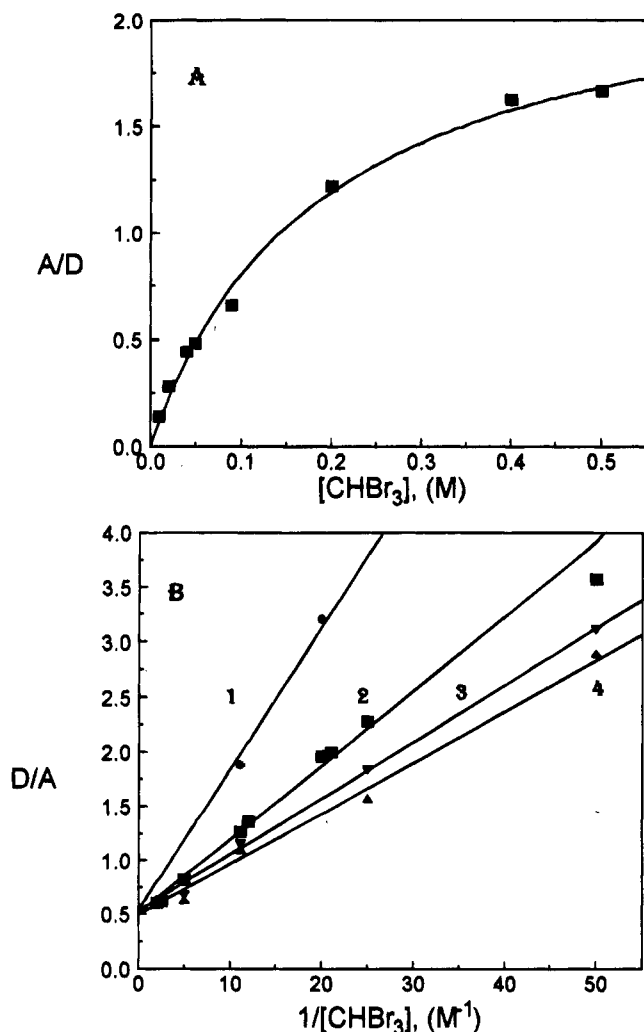
Indeed, a short-lived transient absorption with  $\lambda_{\max} = 338$  nm has been observed in addition to time-dependent absorption of TPN in laser pulse photolysis of the solution of **Ib** in hexane in the presence of  $\text{CHBr}_3$ . Decay kinetics of this transient absorption, A, is shown in Figure 2a (2). We have also verified that this transient absorption is not related to photochemical transformations of  $\text{CHBr}_3$ , which also has a weak absorption at the wavelength of laser irradiation (308 nm). Evidently, the transient absorption at 338 nm could not be ascribed to  $\text{Me}_2\text{Si}$  itself, since it is absent during the laser pulse photolysis of **Ib** without  $\text{CHBr}_3$ .

It is necessary to note that we know nothing about the stability of the hypothetical product of  $\text{Me}_2\text{Si}$  insertion into the C–Br bond of bromoform ( $\text{BrMe}_2\text{SiCHBr}_2$ , **II**), which is absent in both NMR and GC/MS spectra. However, the location of the absorption ( $\lambda = 338$  nm) which is typical for dimethylsilylene complexes with Lewis bases (300–340 nm)<sup>19,30</sup> also speaks in favor of the  $\text{Me}_2\text{Si}$  complex with  $\text{CHBr}_3$ ,  $[\text{Me}_2\text{Si} \cdots \text{CHBr}_3]$ , rather than the insertion product whose spectrum, similar to the majority of brominated organosilicon compounds, is expected to be shifted to the far UV region ( $\lambda_{\max} < 300$  nm) and have rather low extinction coefficients.<sup>20</sup> To study the nature of the observed transient absorption at  $\lambda = 338$  nm, the following kinetic measurements have been performed.

The stationary absorption D (see Figure 2), as for photolysis without  $\text{CHBr}_3$ , is defined by the formation of TPN. Thus, the magnitude of D may serve as a quantitative reference to estimate the relative yield of  $[\text{Me}_2\text{Si} \cdots \text{CHBr}_3]$ . Figure 3A shows the dependence of the A/D ratio on  $\text{CHBr}_3$  concentration. Saturation at high  $\text{CHBr}_3$  concentrations corresponds to the case when all generated dimethylsilylene molecules are consumed by bromoform.

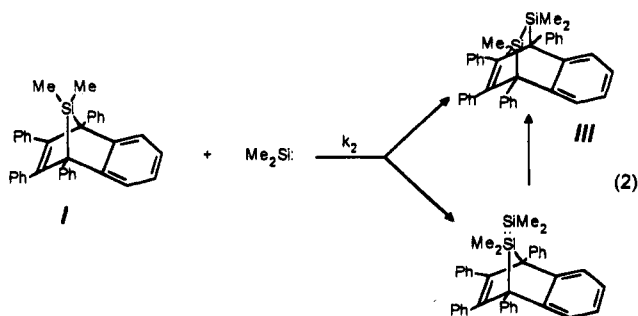


The existence of A/D dependence on  $\text{CHBr}_3$  concentration testifies to the presence of a competitive pathway for dimethylsilylene decay. The insertion of  $\text{Me}_2\text{Si}$  into the endocyclic C–Si bond of strained 7-silanorbornadiene (**Ib**), resulting in 7,8-disilabicyclo[2.2.2]octadiene derivatives (**III**), is the most



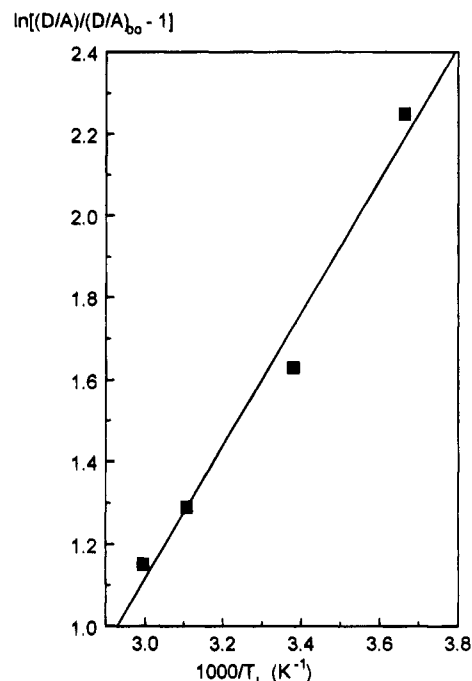
**Figure 3.** (A) Relative yield of signal A (Figure 2a) during laser pulse photolysis of hexane solutions of **Ib** with various bromoform concentrations at  $T = 296$  K. (B) Anamorphosis of the relative yield  $D/A \sim 1/[CHBr_3]$ : (1–4) solution temperatures 273, 296, 322, and 332 K, respectively. (See the meaning of A and D in Figure 2a and in the main text.)

probable reaction (2). This process is also known for the similar



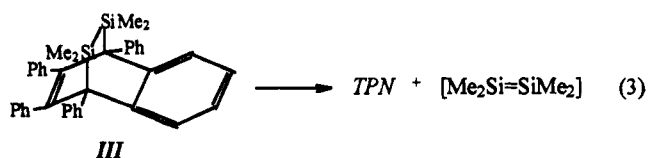
reaction of  $Me_2Ge$  with 7-germanorbornadiene both in solutions<sup>6,7</sup> and in the solid state.<sup>21</sup> The formation of a complex between nucleophilic  $Me_2Si$  and **Ib** could precede the origination of **III**. Indeed, such complexes between nucleophiles and **Ib** were suggested as the key step of nucleophile-assisted endocyclic C–Si bond cleavage in 7-silanorbornadienes.<sup>22</sup>

The absence of **III** in the NMR spectra both under irradiation and after reaction makes it reasonable to assume that this compound is unstable under UV light. It is known that 7,8-disilabicyclo[2.2.2]octadienes may be subjected to photochemical or thermal decomposition (3), leading to corresponding



**Figure 4.** Temperature dependence of the ratio of reaction rate constants  $k_2/k_1$  calculated with the data of Figure 3B using eq 5.

aromatic hydrocarbons and organosilicon species resulting from disilene transformations:<sup>23,24</sup>



Note that analysis of the reaction products with NMR and GC/MS has shown that the main products of photolysis of **Ib** in the presence of  $CHBr_3$  (1:12) are silicon-containing oligomers along with moderate (ca. 10%) quantities of  $Me_2SiBr_2$ ,  $CH_2Br_2$ , and  $CHBr_2-CHBr_2$ . Under our experimental conditions the formation of oligosilanes is most probably due to the disilene transformations, e.g.

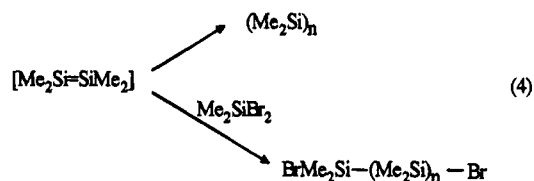
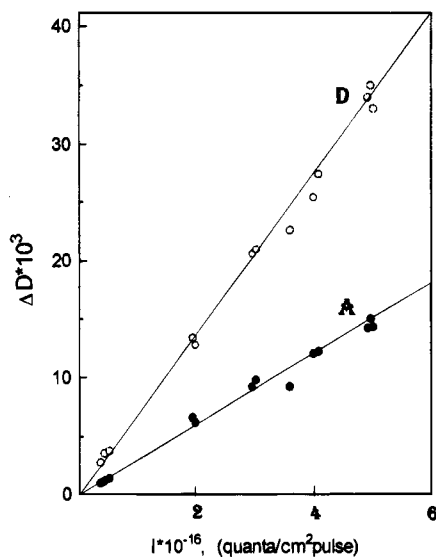


Figure 3B shows the anamorphosis of the yield of the observed signal  $D/A$  vs  $1/[CHBr_3]$  in accordance with the simple competitive kinetic scheme (eqs 1 and 2),

$$D/A = (D/A)_\infty (1 + k_2[I]/k_1[CHBr_3]) \quad (5)$$

These dependencies allow one to calculate the ratio of reaction rate constants,  $k_2/k_1$ . Parameter  $(D/A)_\infty$  the intercept of the ordinate axis at  $1/[CHBr_3] \rightarrow 0$ , is equal to the ratio of extinction coefficients of TPN and the  $[Me_2Si \cdots CHBr_3]$  complex. At room temperature (296 K)  $k_2/k_1 = 130$ ; i.e., the reaction of  $Me_2Si$  with **Ib** is at least 2 orders of magnitude faster than that with  $CHBr_3$ . The measurements of  $k_2/k_1$  at various temperatures (Figure 4) show that these reactions have very similar preexponential factors ( $k_2^0/k_1^0$  about 0.7), and the activation energy for reaction with bromoform is greater than that with **Ib** ( $\Delta E_a$  ca. 3.1 kcal/mol).



**Figure 5.** Dependence of the signals A and D (Figure 2a) on the laser pulse intensity. (See the detailed explanations on A and D in the main text).

The effective rate constant for the formation of signal A (Figure 2a (2)) is defined by both reactions 1 (the formation of the complex) and 2, because dimethylsilylene is consumed in both processes:

$$k_{\text{eff}} = k_1[\text{CHBr}_3] + k_2[\text{I}] \quad (6)$$

Since the  $k_2/k_1$  value has been already estimated above,  $k_{\text{eff}}$  (at fixed concentrations of bromoform and **Ib**) allows one to calculate  $k_1$  and  $k_2$  from (6):

$$k_1 = (4.4 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \quad k_2 = (5.7 \pm 1.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (7)$$

The value of  $k_2$  is very close to the diffusion-limited rate constant ( $k_{\text{diff}} = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in hexane) and is in good agreement with reference data for similar complexes.<sup>30</sup>

The intercept  $(D/A)_{\infty} = 0.56$  (Figure 3B) provides a means to estimate the extinction coefficient of the  $[\text{Me}_2\text{Si} \cdot \cdot \text{CHBr}_3]$  complex ( $\epsilon_c$ ) using that of TPN ( $\epsilon_{\text{TPN}} = 720 \text{ M}^{-1} \text{ cm}^{-1}$ ) at  $\lambda = 334 \text{ nm}$ :

$$\epsilon_c = \epsilon_{\text{TPN}}/0.56 = 1280 \text{ M}^{-1} \text{ cm}^{-1} \quad (8)$$

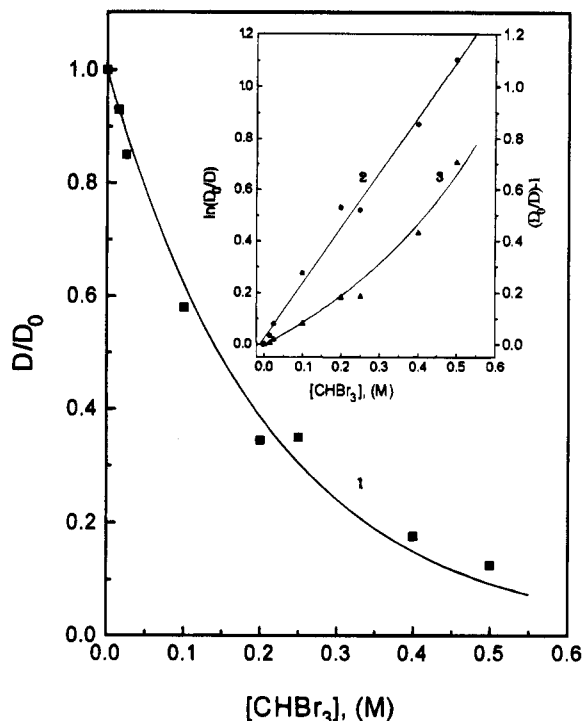
D and A are linearly dependent on the intensity of the laser pulse (Figure 5). Using the value of  $\epsilon_{\text{TPN}}$ , from the dependence of D on laser pulse intensity, one may easily determine the quantum yield of TPN formation in the absence of  $\text{CHBr}_3$ . It is equal to  $0.95 \pm 0.1$ .

Addition of bromoform results not only in the appearance of signal A (Figure 2a (2)) but also in the decrease of TPN yield (D value). This is evidence of quenching of the excited state of initial 7-silanorbornadiene **Ib**. Figure 6 shows the dependence of  $D/D_0$  on  $\text{CHBr}_3$  concentration, where  $D_0$  is the absorption of TPN in the absence of  $\text{CHBr}_3$ . The inset in this figure demonstrates that these data are fairly linear in the coordinates of the Perrin equation

$$\ln(D/D_0) = \Omega[\text{CHBr}_3] \quad (9)$$

in contrast to Stern–Volmer dependence

$$[(D/D_0) - 1] = k\tau[\text{CHBr}_3] \quad (10)$$



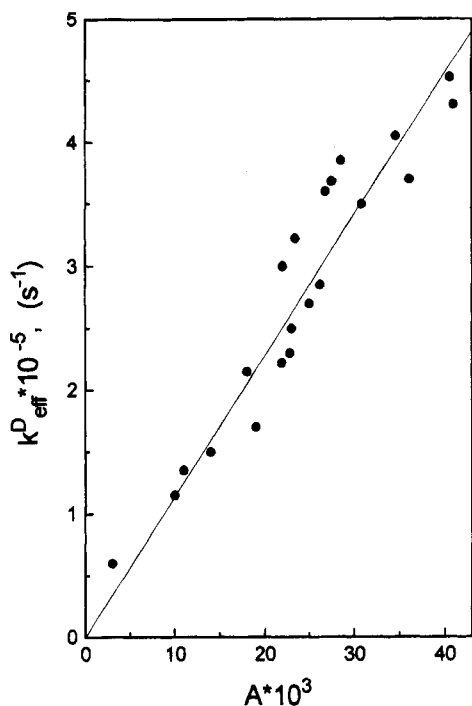
**Figure 6.** Quenching of the photochemical yield of TPN formation (signal D in Figure 2a) by bromoform. (1) Dependence of the relative yield of D on the bromoform concentration. Inset: (2) data processing in accordance with the Perrin equation (8); (3) Stern–Volmer plot (9). (See the detailed explanations on D in the main text.)

where  $\Omega = (4\pi/3)R^3$  is the volume of the quenching sphere,  $k$  is the quenching rate constant, and  $\tau$  is the lifetime of the excited state of **Ib** in the solution without bromoform. In this case, the quenching radius  $R$  is equal to  $11.7 \text{ \AA}$ . This is very close to the contact radius of the partners  $R_0$  (taking into account the bond lengths and covalent radii,  $R_0$  is about  $10.8 \text{ \AA}$ ). Obviously, the realization of the Perrin equation (usually characteristic for static quenching in frozen glassy matrices or solid polymers) for the liquid phase points to a very short lifetime of the excited state of 7-silanorbornadiene (**Ib**) ( $\tau \approx 10^{-12} \text{ s}$ ). Perhaps, under these circumstances, the diffusion of quencher molecules does not manifest itself, and the common Stern–Volmer dependence for liquid solutions transforms into Perrin's one. Short lifetimes of the excited state of **Ib** together with a high quantum yield of photodecomposition are further proofs of  $\text{Me}_2\text{Si}$  generation from the primary singlet excited state of 7-silanorbornadiene. This conclusion fully confirms the statement made on the basis of  $^1\text{H}$  CIDNP analysis (see Scheme 1).<sup>3</sup>

The decay of transient absorption attributed to  $[\text{Me}_2\text{Si} \cdot \cdot \text{CHBr}_3]$  is fairly well approximated by second-order kinetics. Figure 7 shows the linear dependence of the effective rate constant of the signal A decay,  $k_{\text{eff}}^D$ , on its starting amplitude. Independently of the reaction order, the effective rate constant could be defined as follows

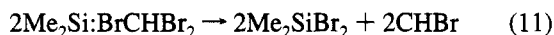
$$k_{\text{eff}}^D = - \left. \frac{1}{C_0} \frac{dC}{dt} \right|_{t=0}$$

where  $C_0$  is the initial concentration of the intermediate (or starting intensity of its absorption signal). In the case of first-order reaction,  $k_{\text{eff}}^D = K_{\text{mono}}$ ; for the second-order process,  $k_{\text{eff}}^D = K_{\text{bim}}C_0$ . If the species under study disappears in both first- and second-order processes,  $k_{\text{eff}}^D = K_{\text{mono}} + K_{\text{bim}}C_0$ . The linear dependence in Figure 7 passes through the origin of coordinates and, therefore, clearly describes the pure second-order reaction.



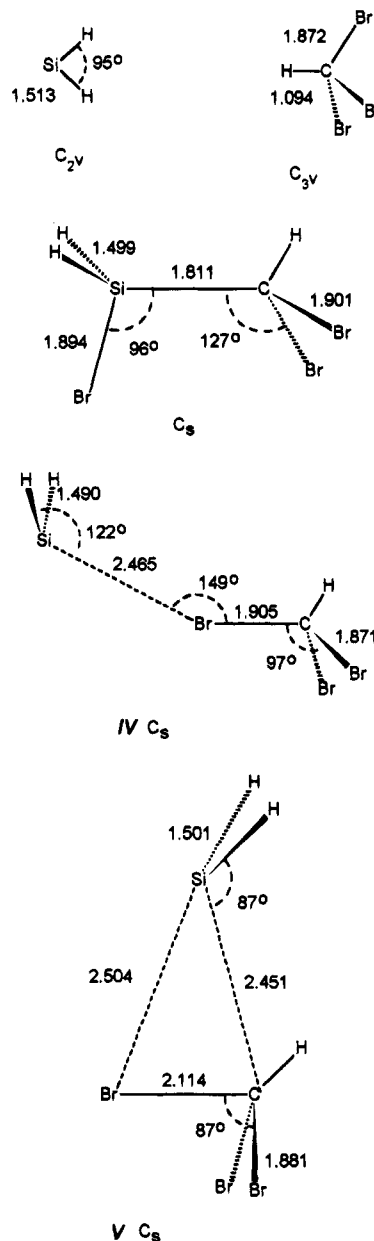
**Figure 7.** Dependence of the effective rate constant,  $k_{\text{eff}}^D$ , of signal *A* decay ( $[\text{Me}_2\text{Si} \cdots \text{CHBr}_3]$  complex, Figure 2a) on the laser starting intensity at  $T = 296$  K. (Details on  $k_{\text{eff}}^D$  definition are in the main text.)

In these experiments, to vary the initial concentration of the  $[\text{Me}_2\text{Si} \cdots \text{CHBr}_3]$  complex, we have used laser pulses with different light intensities. The slope of the dependence in Figure 7 allows one to define the bimolecular rate constant of  $[\text{Me}_2\text{Si} \cdots \text{CHBr}_3]$  decay ( $2k = k_{\text{eff}}^D/C$ ). Concentration  $C$  was calculated from the above determined extinction coefficient of the complex  $\epsilon_c$  and finally we obtained  $2k = 1.61 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Bimolecular decay with similar values of reaction rate constants is also known for the dimethylgermylene  $\text{Me}_2\text{Ge}$  complex with triphenylphosphine  $\text{Ph}_3\text{P}^{25}$  and  $\text{Me}_2\text{Si}$  complexes with O-, N-, S-, and P-containing species.<sup>30</sup> In our case, taking into account a set of products of the brutto reaction, one may suggest the following processes:



Indeed, the formation of the product of CHBr insertion into the C–Br bond of  $\text{CHBr}_3$ , the 1,1,2,2-tetrabromoethane (along with  $\text{Me}_2\text{SiBr}_2$ ), was detected by GC/MS and  $^1\text{H}$  NMR spectral data. Our PM3 calculations of the model reaction have shown that reaction 11 should be energetically favorable (see below). Thus, the transient species with  $\lambda_{\text{max}} = 338$  nm have absorption bands and formation and decay rate constants closely approximating those of the donor–acceptor complexes of  $\text{Me}_2\text{Si}$  and  $\text{Me}_2\text{Ge}$  with Lewis bases. This supports the above assignment.

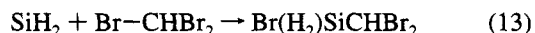
Finally, we would like to compare the results of our laser pulse photolysis study with  $^1\text{H}$  CIDNP data.<sup>3,4</sup> Both methods show that the primary photoexcited state of **Ib** is  $S_1$ . Moreover, the results of the pulse photolysis study provide some indirect evidence concerning the structure of a biradical, the precursor of dimethylsilylene (see Scheme 1). The observation of  $^1\text{H}$  CIDNP effects<sup>4</sup> in the system under study is possible only in the case of a negligible electron exchange interaction in the intermediate biradical. Small exchange integrals in 1,3-biradicals may be explained by the orthogonal orbitals of two unpaired electrons. This means that transformation from the initial **Ib**



**Figure 8.** PM3-calculated stationary points considered in the study for reaction 14. Bond lengths are in angstroms, and bond angles are in degrees.

to a radical is accompanied by significant distortion of geometry. One can assume that this distortion of geometry should result in the irreversibility of photodecomposition of **Ib**. Indeed, the quantum yield for the photolysis of **Ib** is close to 1. Thus the data on the mechanism of photolysis of 7-silanorbornadiene (**Ib**) obtained by  $^1\text{H}$  CIDNP and laser pulse photolysis techniques are mutually complementary.

To elucidate a possible mechanism of the reaction between  $\text{SiH}_2$  and bromoform, we have carried out semi-empirical quantum chemical PM3 calculations of the model reaction between a singlet  $\text{SiH}_2$  and bromoform:



The structures of the stationary points of the reaction (12) are presented in the Figure 8. We find that the first stage of the insertion reaction (12) is the formation of a loose complex **IV** of  $C_s$  symmetry. It lies 23.3 kcal/mol below the isolated  $\text{SiH}_2$  and  $\text{CHBr}_3$ . Analysis of the electronic structure of complex **IV** shows that it is stabilized by interaction between a

vacant p-MO of the silylene and a lone electron pair of the reacting bromine atom. Similar but less stable types of complexes were found earlier in *ab initio* calculations<sup>26</sup> of the silylene reactions with hydrogen fluoride and hydrogen chloride.

A characteristic feature of complex **IV** is noticeable charge transfer from bromoform to the SiH<sub>2</sub> moiety (totally -0.023 e). Moreover, a significant polarization in the CHBr<sub>3</sub> fragment of **IV** takes place. In particular, a strong positive charge (+0.2 e) is formed on the bromine atom interacting with the silylene molecule. Such a strong polarization could finally cause a positive bromine atom abstraction from CHBr<sub>3</sub> by SiH<sub>2</sub> with the formation of an ion pair H<sub>2</sub>Si<sup>+</sup>BrI<sup>-</sup>CHBr<sub>2</sub>.

One can consider two main pathways for the further transformation of complex **IV**: its rearrangement into the insertion product and the extrusion of CHBr species.

Rearrangement of **IV** into Br(H<sub>2</sub>)SiCHBr<sub>2</sub> takes place via the transition state **V** of C<sub>s</sub> symmetry. The activation barrier for this process is rather high (22.3 kcal/mol). Thus the calculations predict that complex **IV** should be rather stable regarding both the dissociation to the starting silylene and bromoform and further rearrangement into the insertion product. Since the formation of **IV** takes place without an activation barrier, it is reasonable to suggest that in the excess of bromoform all forming silylenes would be bound into complexes **IV**.

To explain the second-order kinetics experimentally observed for the decay of the Me<sub>2</sub>Si<sup>••</sup>BrCHBr<sub>2</sub> complex, a model bimolecular reaction (14) was considered.



The reaction is calculated to be slightly exothermic (8.6 kcal/mol). Theoretical study of the detailed mechanism of (14) is underway.

## Conclusions

In the present work we were not able to detect dimethylsilylene upon laser pulse photolysis of 7-silanorbornadiene (**Ib**). However the formation of a transient species with an absorption maximum at 338 nm was observed when the photolysis was carried out in the presence of CHBr<sub>3</sub>. This band was tentatively assigned to the molecular complex between dimethylsilylene and bromoform. The results of semi-empirical PM3 calculations also predict the formation of a rather stable complex between SiH<sub>2</sub> and CHBr<sub>3</sub>. Such complexes with halogen-containing donors have also been observed for germylenes in low-temperature matrices.<sup>27</sup> The formation of complexes between silylenes and halogenated organic species has been suggested as the first step of the reaction.<sup>1</sup> This paper provides the first spectral evidence for the existence of such a complex in the liquid phase with a halogenated species, CHBr<sub>3</sub>, the latter not only being a complex substrate but also being responsible for the chemical reaction with silylene.

**Acknowledgment.** The financial support of the Russian Foundation for Fundamental Research is gratefully acknowledged (Research Grants Nos. 93-03-5026, 93-03-5452, and 94-03-08975).

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