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Paramagnetic intermediates in the photolysis of 7-silanorbornadiene studied by means of spin chemistry method

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Abstract

The influence of an external magnetic field on the yield of photo-decomposition products of 7,7′-dimethyl-7-silanorbornadiene derivative has been detected in laser pulse photolysis experiments. The observations of magnetic field effects alterations in the presence of scavengers, O_2 and PPh_3, in combination with ^{1}H-CIDNP data form the basis for the identification of the structure of paramagnetic intermediates involved in the process. It has been shown that magnetic field effects originate in biradical intermediates. These species result from both endocyclic Si–C bond cleavage in the initial compound and the reaction of dimethylsilylene (in a singlet or a triplet excited state) with starting 7-silanorbornadiene. To explain the influence of O_2 upon the magnetic field effects, the reversible formation of oxygen complex with biradical species has been suggested. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Magnetic field effect; CIDNP; Biradicals; Oxygen complexes; Dimethylsilylene

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1. Introduction

Heavy carbene analogs, silylenes, germylenes and stannylenes, are the important reactive intermediates in a number of chemical reactions [1–4]. In the last decade, these short-lived species have become a subject of growing interest. The derivatives of 7-sila(germa)norbornadienes play a significant role as convenient precursors of carbene analogs generated upon thermolysis or photolysis [1,2,4,5]. However, only a few attempts were made to apply the physico-chemical methods, including laser pulse photolysis [6] and chemically induced dynamic nuclear polarization (CIDNP) techniques [7–12] to study the mechanisms of silylene and germylene generation from these heterocycles, as well as the mechanisms of their insertion and cycloaddition reactions. The results of quantum–chemical calculations indicate that carbene analogs are ground state singlets [1,2,13,14], but the experimental data on the multiplicity of the reactive states of these species are still scarce [7–12]. There is a lack of reference data on the reactivity of triplet excited silylenes and germylenes.

The following scheme of photo-decomposition of 7,7′-dimethyl-7-silanorbornadiene (**I**) has been proposed on the basis of both ^{1}H-CIDNP and laser pulse photolysis studies [6] (Scheme 1).

The involvement of paramagnetic species (singlet and triplet biradicals of **I** and triplet dimethylsilylene) in this photoreaction is still a matter of dispute [2,15]. An unambiguous conclusion on the participation of the radical species in this process might be drawn based on the findings of a magnetic field effect (MFE) study. In

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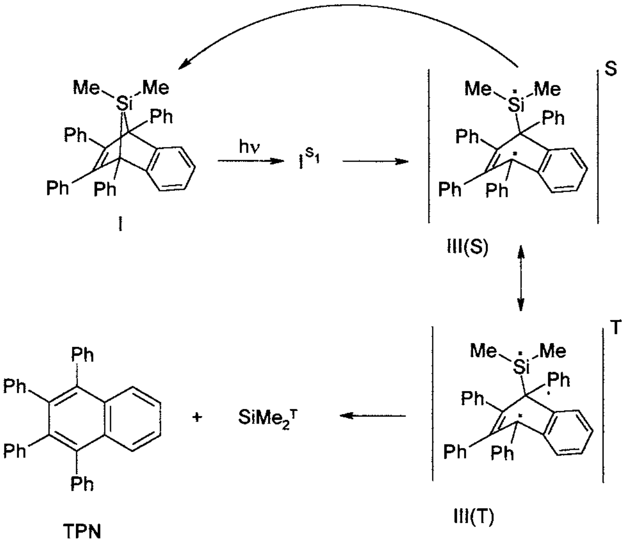
principle, the analysis of the character of MFE-dependence and the sign of the magnetic field effect provide the means for independent definitions of both the multiplicity of the reactive state and the structure of paramagnetic precursors of the reaction products. The present paper discusses the results from the application of the MFE method to the investigations of the photolysis of 7-silanorbornadiene, **I**.

2. Experimental

7,7′-Dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene **I** was synthesized according to an earlier procedure [16]. PPh_3 (99%, Aldrich) was used without additional purification The solvents (*n*-hexane, cyclo-C_6D_{12}, C_6D_6 and CD_2Cl_2) were dried and purified by conventional techniques [17]. All experiments were carried out at ambient temperature.

The set-up for laser flash photolysis experiments includes excimer XeCl laser ($\lambda = 308$ nm) with a pulse energy ca. 10 mJ, pulse duration 15 ns, delay time 50 ns. Angle between the excitation and probing light beams is ca. 2°. A detailed description of the set-up can be found elsewhere [18].

Experiments were performed in 1 cm-optical quartz cells. The concentration of **I** (typically ca. 1×10^{-3} M) was controlled spectrophotometrically ($\varepsilon_{308} = 2 \times 10^3$ M^{-1} cm^{-1}) by a Specord UV-VIS spectrophotometer. In all experiments, the wavelength of probing light was 334 nm. With the exceptions mentioned below, samples were deaerated by 15 min of Ar bubbling. Photo-decomposition of **I** was monitored by the yield of a stable end product of the reaction, 1,2,3,4-tetraphenylnaphthalene (TPN). Below, the change of its optical density is designated as ΔD. All experimental results were normalized with respect to laser pulse intensity.



Scheme 1.

The external magnetic field was applied by means of a specially designed permanent Sm–Co magnet, with variable distances between the poles. The geomagnetic field was assumed to be close to a zero level. The MFE was defined as the ratio of TPN yield under the action of the external magnetic field (ΔD_H) to that under the geomagnetic one (ΔD_0):

$$\mathrm{MFE} = \frac{\Delta D_0 - \Delta D_H}{\Delta D_0} \times 100\%$$

This expression shows that MFE > 0, if the yield of TPN decreases in the external magnetic field ($\Delta D_H < \Delta D_0$); accordingly, MFE < 0 reflects the growth of TPN yield in the external magnetic field ($\Delta D_H > \Delta D_0$).

Data points of the MFE dependencies show the results of standard statistical processing of 7–10 kinetic traces. The error bars represent the S.D.

NMR spectra were taken using a JEOL JNM FX90Q spectrometer (^1H operating frequency 90 MHz) equipped with a photochemical device for sample irradiation directly in the probe of the spectrometer. The light source employed was a high pressure Hg lamp (DRSh-1000 of 1 kW power) with a thermal filter. The concentration of **I** was varied in the range from 10^{-3} to 10^{-1} M. Samples with equilibrium concentrations of O_2 were used; PPh_3 was taken in 2–5-fold excess.

Attempts to study CIDNP in low magnetic fields were carried out using a Bruker AM 300 NMR spectrometer (^1H operating frequency 300 MHz) equipped with a specially designed continuous flow system. The solution of **I** (5×10^{-3} M in C_6D_6) has been irradiated by a sequence of laser pulses (excimer laser, $\lambda = 308$ nm, pulse frequency is equal to 20 Hz, pulse duration was 20 ns, pulse energy amounts to 40 mJ) in a separate magnet with a variable magnetic field strength ranging from 100 to 2100 G. After irradiation, the solution was transferred to the probe of the NMR spectrometer by means of the flow system. The shortest time of transfer was ca. 1 s. Apparently, failure to observe CIDNP effects within this magnetic field range was related to very small relaxation times of the methyl protons of **I**. Independent measurements have shown that this time is equal to 0.8 s, which is even smaller than the characteristic time of sample transfer by means of a flow system.

3. Results and discussion

In laser pulse photolysis experiments, the yield of TPN formed upon photo-decomposition of **I** was found to depend on the external magnetic field (MF) strength and the presence of the scavengers, O_2 and PPh_3, in the reaction mixture. Fig. 1 presents the typical kinetic traces of TPN absorbance observed in MF of different strengths.

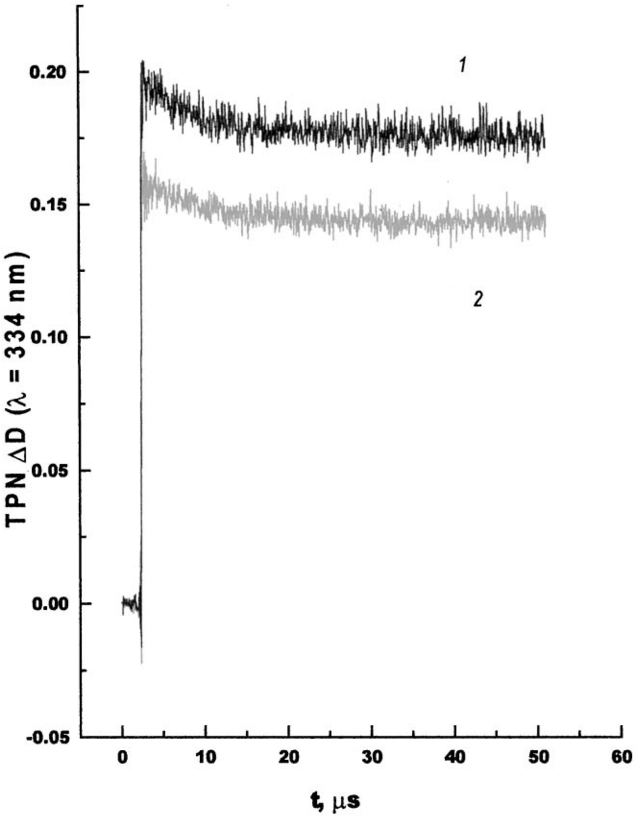


Fig. 1. The time profile of the absorbance of TPN measured during the photolysis **I** in the presence of O_2. (1) in geomagnetic field; (2) at 540 G.

Figs. 2 and 3 show the dependencies of the MFE on the external MF strength detected under various experimental conditions. Thus, Fig. 2 shows MFE dependencies observed in the photolysis of **I** in aerated and deaerated solutions. MFE dependencies presented in Fig. 3 were obtained in the presence of a Lewis base, PPh_3. Lewis bases (e.g. ethers, amines, phosphines, sulfides) are known to form complexes with silylenes; such complexes were previously studied by experimental [19] and theoretical [20] methods. Therefore, in the system under study, PPh_3 plays a role of the trapping agent for the dimethylsilylene, which is another product of the photolysis of **I**. The relative yields of TPN formed during the photolysis of **I** in the presence of various scavengers are listed in Table 1.

The photolysis of **I** was also studied by ^{1}H-NMR and ^{1}H-CIDNP techniques in cyclo-C_6D_{12}, C_6D_6 and CD_2Cl_2 solutions. ^{1}H-NMR spectral data clearly testify to the formation of 7,7′,8,8′-tetramethyl-1,4,5,6-tetraphenyl-2,3-benzo-7,8-disilabicyclooctadiene (**II**) resulting from the photolysis of **I**. The compound **II** is a product of Me_2Si insertion into the endocyclic Si–C bond of starting **I** (Scheme 2):

The maximum yield of **II** was detected in CD_2Cl_2 under the irradiation with the full light of high pressure Hg lamp. In this case, the CIDNP effects were detected for the protons of **I**, **II** and TPN (Fig. 4). Chemical shifts of the initial compounds and the reaction products as well as the signs of ^{1}H-CIDNP effects are given in Table 2.

According to modern understanding, the influence of the external MF on the reaction rate or the yield of the reaction products is a reliable evidence of the prevalent participation of paramagnetic precursors. Thus, MFEs detected in the formation of TPN during the photolysis of deaerated solutions of **I** confirm the earlier proposed reaction mechanism (Scheme 1) [6,7,21].

Indeed, in the framework of the existing theories [22] it is very difficult to explain the extremes of MFE dependencies located at several hundred Gauss (see Figs. 2 and 3) without the biradical species taken into account. In a general case, the position of the extremes correlates with the value of mixing parameter which affects the process of S–T conversion, and virtually determines the MFE magnitude. Typically, the mixing efficiency is defined by effective hyperfine interaction (HFI) in the radical pair ($A_{\mathrm{eff}} = \sqrt{\Sigma_i A_i^2}$), by $\Delta g H_0$ term (Δg is the difference of g-factors of the radicals in a radical pair, H_0 is the external MF strength), or by the energy of the effective electron exchange interaction (J).

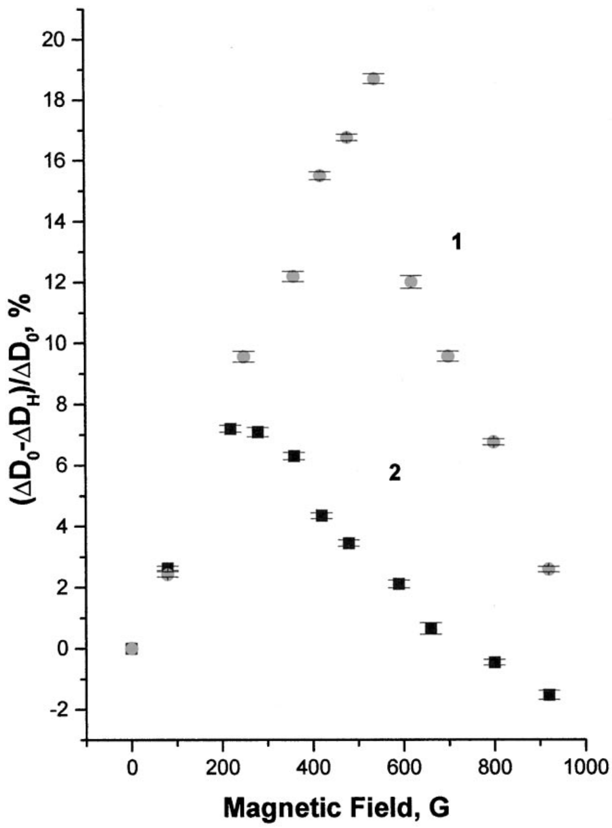


Fig. 2. Magnetic field effect on TPN yield observed in the photolysis of **I** in aerated and deaerated solutions: (1) in aerated solution; (2) in the absence of O_2.

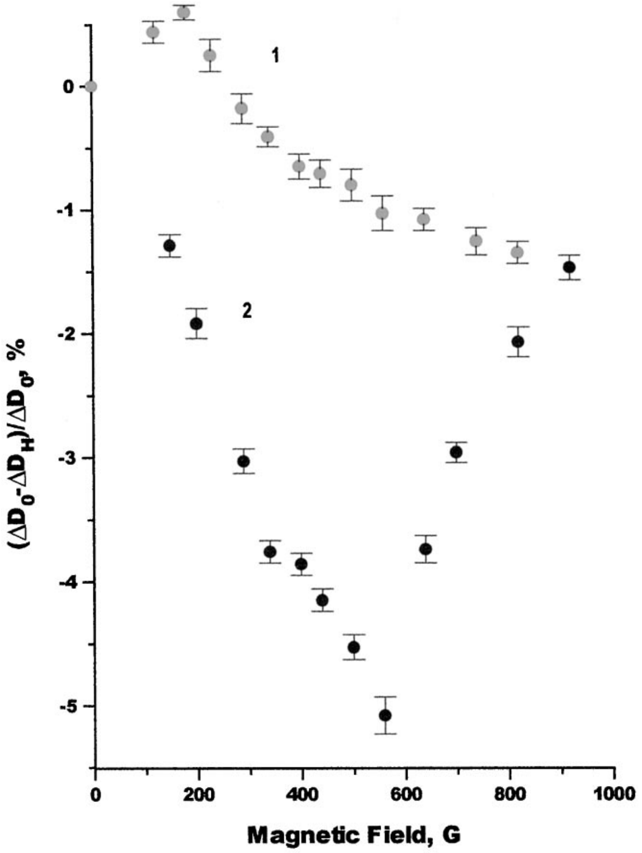


Fig. 3. Magnetic field effect on TPN yield observed in the photolysis of **I** in aerated and deaerated solutions in the presence of 2×10^{-3} M of Ph_3P: (1) in deaerated solution; (2) in the presence of O_2.

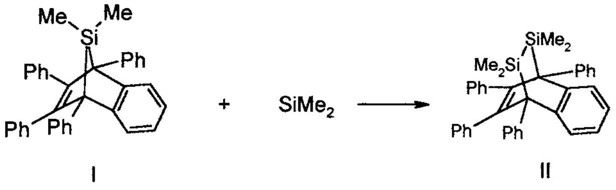
In the reaction under study, for any feasible radical pair comprised of silicon- and carbon-centered free radicals, the values of HFI and ΔgH_0 terms are not greater than several Gauss. Thus, the field dependence of the MFE, if only formed via HFI- and Δg-mechanisms, should not demonstrate any extremes within the external magnetic field range under study.

On the other hand, CIDNP effects detected for the methyl protons of the starting **I** suggest the formation of biradical intermediate which is a paramagnetic precursor of the polarized species. Note also that the positions of the extremes of the experimental MFE dependencies (Figs. 2 and 3) are in the range characteristic for the electron exchange interaction values of J, which are quite typical for biradicals (250–500 G) [22].

Table 1
The relative yield of TPN in the photolysis of 7-silanorbornadiene **I** in the presence of various scavengers[a]

Scavenger	TPN yield (%)
O_2 (equilibrium concentration, ca. 2×10^{-3} M)	85
$O_2+2\times10^{-3}$ M PPh_3	75
$O_2+0.1$ M $CHBr_3$	57

[a] The yield of TPN in the photolysis of **I** in the absence of scavengers was set to 100%.



Scheme 2.

The manifestation of $S-T_0$ mechanism of CIDNP formation in the reaction under study [7] by no means is at variance with the assumption on the formation of biradical intermediates. It is known that in high magnetic fields polarizations in rigid biradicals are generated only via $S-T_0$ mechanism [22]. Unfortunately, due to short longitudinal relaxation times of the methyl protons of **I** (see Section 2) it was not possible to measure the dependence of CIDNP effects versus external MF strength, which is commonly accepted criterion for the detection of biradical species.

However, the observed influence of the scavengers on the yield of TPN points to a more complex process of TPN formation than that proposed in Scheme 1. For example, the dependence of TPN yield on PPh_3 concentration (Fig. 5, Table 1) suggests that TPN could result not only from the decomposition of the biradical **III** shown in Scheme 1, but also after the reactions of dimethylsilylene in the bulk, since it is Me_2Si that forms a donor–acceptor complex with PPh_3 [19,20].

As it has been already mentioned, laser pulse photolysis experiments [6] as well as ^{1}H-NMR spectral data of the present paper have unraveled the reaction between Me_2Si and the initial **I** leading to disilabicyclooctadiene derivative **II** (Scheme 2). The dependence of TPN yield on Ph_3P concentration (Fig. 5) allows one to suggest that TPN also results from the interaction of **I** with Me_2Si. The higher the concentration of PPh_3 is, the lower the fraction of 'free' Me_2Si that will attack initial **I**, leading ultimately to the formation of TPN. CIDNP effects for methyl and phenyl protons of **II** (Fig. 4 and Table 2) indicate that the reaction of **I** with Me_2Si also includes the stages with paramagnetic precursors. Similar to Scheme 1, the process could be written as below (Scheme 3).

Scheme 3 shows the case of the reaction between **I** and the excited triplet state of Me_2Si. Indeed, the rate constant of the reaction between Me_2Si and **I** measured earlier by laser pulse photolysis method [6] approaches the diffusion control limit and equals 5.7×10^9 M^{-1} s^{-1}. The value is quite characteristic for the reactions of triplet carbenes [23]. ^{1}H-CIDNP technique has allowed the detection of several reactions of singlet Me_2E (E = Si, Ge) species [7–10]; however, two cases of the excited triplet dimethylsilylene reactions with thiacycloheptyne [11] and carbon tetrachloride [12] were also reported.

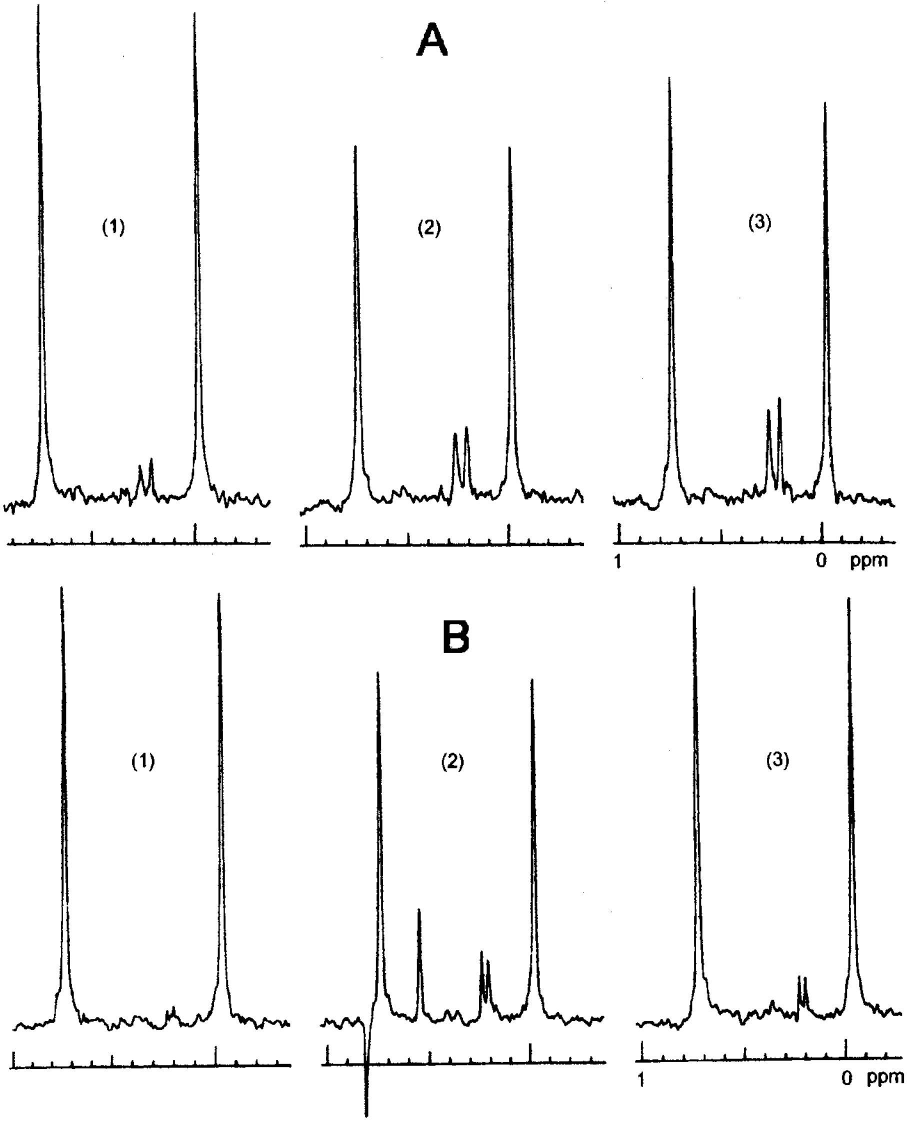


Fig. 4. ^{1}H-CIDNP spectra observed in the photolysis of **I** in CD_2Cl_2 in the presence (A) and in the absence (B) of Ph_3P (only aliphatic part is shown). (1) initial spectrum; (2) spectrum under irradiation; (3) dark spectrum after irradiation.

According to the MFE theory [22], the alteration of MFE sign under different reaction conditions indicates that the initial paramagnetic precursors of the end products (in our case, TPN) have an opposite multiplicity. Therefore, the observation of MFE dependencies of TPN yield with the opposite signs in the absence and in the presence of PPh_3 (Figs. 2 and 3) confirms the possibility of participation of both triplet and singlet states of Me_2Si in the reaction with the initial 7-silanorbornadiene **I**. As it has been already mentioned, CIDNP [7] and laser pulse photolysis [6] data solely favored the formation of the initial singlet biradical **III(S)** from 7-silanorbornadiene (Scheme 1). Therefore, it is quite reasonable to suggest that the triplet paramagnetic precursors could result from the reaction of the triplet Me_2Si with the initial **I**.

Thus, in the reaction under study, it is possible to point out three biradical precursors of TPN: the initial singlet biradical **III(S)** and biradicals of disilabicyclooctadiene **IV** (both in S and T initial states).

Let us now briefly discuss the expected variations in TPN yield caused by magnetic field influence upon the S–T transitions in the biradicals **IV(S)** and **IV(T)**. For example, if the biradical **IV** is initially formed in the singlet state, the extreme of magnetic field dependence should correspond to the highest possible yield of TPN. Indeed, in this case (see for analogy, Scheme 1), TPN is formed only via the S–T conversion stage, and in accordance with the radical pair (RP) theory, [22] the efficiency of this conversion is greatest in the MF of the order of *J*. On the other hand, the realization of Scheme 3, where the initial multiplicity of biradical **IV**

Table 2
^{1}H-CIDNP effects observed during the photolysis of 7-silanorbornadiene **I** (0.01 M in CD_2Cl_2)

Proton group	Chemical shift δ (ppm)	^{1}H-CIDNP effects	
		In the absence of scavengers	In the presence of Ph_3P (0.1 M)
Me_2Si– (of **I**)	-0.06; 0.72	A	A
TPN	ca. 8.00	A	None
Me_2Si– (of **II**)	0.18; 0.22	A	E
Ph groups (of **II**)	ca. 7.00	A	E (weak)

E, emission; A, absorption.

is triplet, implies the reversed conditions. In this case, TPN originates from the initial triplet state of biradical **IV** and the growth in T–S conversion efficiency results in the decrease in TPN yield.

Taking these facts into account, one might attempt to explain the experimental MFE dependencies observed under various conditions (Figs. 2 and 3; influence of O_2 on the MFE magnitude and the location of the extreme of field dependence will be discussed below). The sign of MFE observed in the absence of PPh_3 points to the prevalence of contribution from the initial triplet biradical precursor of TPN (**IV(T)**). It is observed from Fig. 2 that in this case, the maximum of the field dependence corresponds to the minimum yield of TPN. This fact could be explained only assuming that the MFE formed at the stage of biradical **III** is much lower than that in the case of biradical **IV**.

To explain the sign of the observed MFE it is also necessary to assume that the fraction of biradicals **IV(T)** should be greater than that of the corresponding biradicals **IV(S)**. By this means that the rate of the reaction of Me_2Si^T with the initial 7-silanorbornadiene **I** is comparable with its T–S conversion rate (Scheme 4).

Assuming that the processes shown in Scheme 4 reflect the main transformation pathways of triplet excited Me_2Si^T in the bulk, one can estimate the lifetime of Me_2Si^T. The lifetime τ is determined by the following expression:

$$\tau = \frac{1}{k_{T-S}} + \frac{1}{k_I \cdot [\mathbf{I}]}.$$

In accordance with the above assumption of the comparable rates of T–S intersystem crossing in Me_2Si and its interaction with the starting **I**, $k_{T-S} \sim k_T \cdot [\mathbf{I}]$. Assuming that the earlier estimated rate constant for the reaction of Me_2Si with **I** (5.7×10^9 $M^{-1} s^{-1}$ [6]), is mainly related to k_T, within the range of experimental concentrations of **I** (ca. 10^{-3} M), one can estimate the lifetime of Me_2Si^T:

$$\tau \approx \frac{2}{5.7 \times 10^9 \times 10^3} \approx 3.5 \times 10^{-7}\ \mathrm{s}$$

To verify the inference about the prevailing contribution of triplet Me_2Si reactions to the observed MFE, the photolysis of **I** has been carried out in the presence of PPh_3. At first glance, seemingly paradoxical result has been obtained—the MFE becomes extinct in the deaerated solutions in the presence of PPh_3, and appears again when both PPh_3 and O_2 are present in the reaction mixture. In the latter case, however, the sign of MFE is opposite to that observed during the photolysis in the absence of PPh_3 (Fig. 3).

The essence of the above mentioned paradox lies in the fact that in the presence of PPh_3 one might expect the decrease in the contribution of singlet biradicals to MFE. As it has been already stated, PPh_3 is capable of forming complexes with heavy carbene analogs; however, the formation mechanism for such complexes suggests that complexation occurs only with the singlet species. As far as MFE extinction and alteration of its sign in the presence of PPh_3 and O_2 are concerned, these facts could be explained only under the assumption of PPh_3 interaction with the triplet excited state of Me_2Si, as well. It is seen from Fig. 4 that the dependence of TPN yield on PPh_3 concentration linearizes in the frames of Stern–Volmer plot. Since TPN is also formed in the reaction of Me_2Si^T with **I** (see above reasoning) one might suggest that PPh_3 is capable of quenching the triplet excited state of Me_2Si.

A similar assumption of the interaction of Me_2Si^T with PPh_3 has been made earlier [12] when employing ^{1}H-CIDNP technique to study the photolysis of **I** in the solutions containing CCl_4 in the presence and in the absence of PPh_3. In this case, the reaction of Me_2Si^T with CCl_4 has been observed in the absence of PPh_3, while in the presence of PPh_3 the alteration of the signs of CIDNP effects for the products originating from the radical pair of $Me_2ClSi^{\cdot}$ and $Cl_3C^{\cdot}$ free radicals has been detected (Scheme 5). The most reasonable explanation of these alterations is the decrease in the lifetime of triplet excited state of Me_2Si in the presence of PPh_3. One might assume that this occurs on the encounter of reagents.

The processing of the data on quenching of Me_2Si by PPh_3 (Fig. 5(b)) gives $k \cdot \tau = 200$. The above estimated lifetime of Me_2Si^T leads to a quite reasonable value of quenching rate constant k, ca. 5.7×10^8 $M^{-1} s^{-1}$. In this case, the quenching finally results in the formation of the complex of singlet Me_2Si with PPh_3.

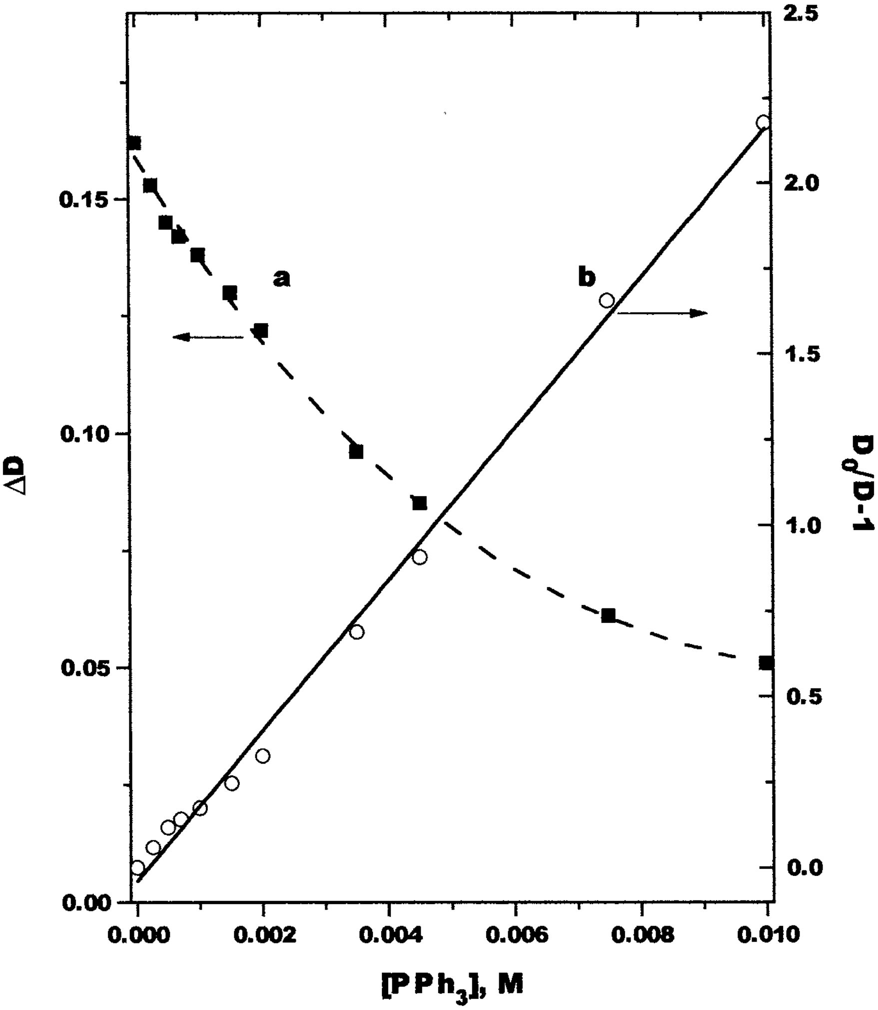


Fig. 5. (a) The dependence of TPN yield on Ph_3P concentration in the photolysis of **I**. (b) Stern–Volmer plot for data of (a).

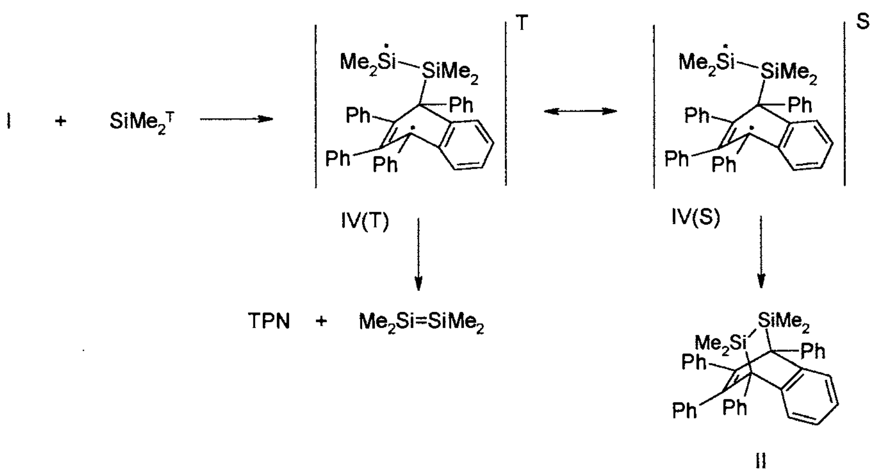
In principle, the observed decrease in TPN yield as well as the disappearance of MFE in deaerated solutions in the presence of PPh_3 could be stipulated by the following. Either Me_2Si in a complex with PPh_3 (similar to the complex of Me_2Ge with PPh_3 [24]) does not enter the reaction with the initial **I**, or this reaction has an alternative mechanism. ^{1}H-NMR and ^{1}H-CIDNP data show that TPN and **II** also arise in the presence of PPh_3, however, in this case, the ratio of these products differs from previous cases. The decrease in TPN yield in the presence of $CHBr_3$ (see Table 1) additionally suggests that complexation changes the reactivity of Me_2Si, since $CHBr_3$ has shown to form complex with Me_2Si [6].

For high PPh_3 concentrations (ca. 0.1 M), the yield of **II** exceeds those of the other reaction products. Note that no magnetic field effect has been observed in laser pulse photolysis experiments as the concentration of PPh_3 increases (Fig. 6). The acceleration of photodecomposition of **I** detected during the direct photolysis in the probe of NMR spectrometer shows that PPh_3 is capable of sensitizing the decay of **I**. Moreover, it is known [25] that PPh_3 is subjected to photo-dissociation:

$$PPh_3 \xrightarrow{h\nu} (PPh_3)^T \rightarrow Ph_2P^{\cdot} + {}^{\cdot}Ph$$

Thus, the absence of MFE at a high concentration of PPh_3 could be stipulated by several reasons.

It is essential to note that ^{1}H-CIDNP effects of **I**, **II**, and TPN (Table 2) were observed in the photolysis of **I** in the presence of PPh_3 in CD_2Cl_2. The analysis of these effects goes beyond the scope of the present paper, since the conditions of CIDNP experiments differ significantly from those of the laser pulse photolysis experiments. However, the observation of CIDNP effects is of great importance by itself. Indeed, nuclear polarization effects show that dimethylsilylene complex also reacts with the initial **I** via the formation of biradical intermediate. Thus, NMR and CIDNP data show that in contrast to dimethylgermylene [24], the complex of Me_2Si with PPh_3 is capable of reacting with the initial silanorbonadiene **I**.



Scheme 3.

The possible ways of TPN formation during the photolysis of **I** are summarized in Scheme 6.

As it has been already mentioned, oxygen has a pronounced impact on the MFEs detected during the photolysis of **I** in the presence or in the absence of PPh_3 (Figs. 2 and 3). For example, the MFE is absent in the presence of PPh_3 in deaerated solutions and is restored in the presence of O_2 (see Fig. 3).

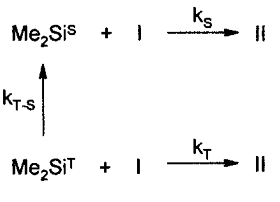
Oxygen is known [26–28] to be an effective trapping agent reacting with triplet and singlet states of biradicals. This interaction is most extensively studied in the photolysis of cyclic and aromatic ketones. The triplet–triplet interaction between triplet biradical (B) and triplet O_2 resulting in singlet biradical and singlet oxygen, as well as chemical reactions of biradicals with both singlet and triplet O_2 were suggested to be as follows:

$$^3B^* + O_2\left(^3\Sigma_g^-\right) \rightarrow {}^1B + O_2(^1\Delta_g)$$

$$^{3,1}B + {}^3O_2\left(^3\Sigma_g^-\right) \rightarrow X$$

$$^{3,1}B + {}^1O_2(^1\Delta_g) \rightarrow Y,$$

where X and Y are the reaction products. The interaction of O_2 with biradicals results in the reaction products containing oxo- and hydroxyl groups and the dioxetane moieties [28].

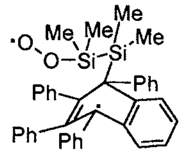


Scheme 4.

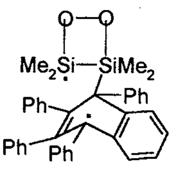
A reversible addition of oxygen to biradicals has been also observed, the process is known [27] to accelerate the consequent fragmentation of the biradicals:

$$B\ldots O_2 \rightarrow X + Y + O_2$$

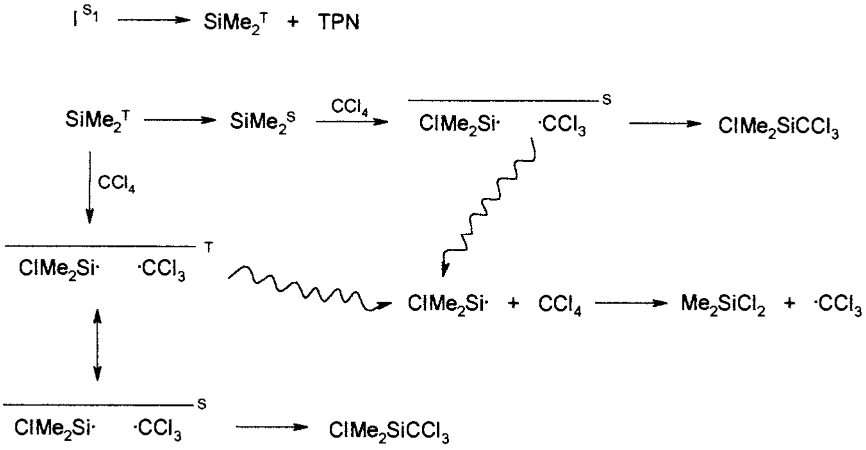
It has been shown earlier [21] that in solution the triplet excited state of analogous 7-germanorbornadiene is quenched by oxygen. It is evident that this excited state corresponds in structure to the biradical species analogous to **III** [7]. In the case under study, the decrease in TPN yield during the photolysis of **I** in the presence of O_2 is also observed (Table 1). At the same time, the MFE is increased by a factor of 2.7, and in the presence of O_2 the extremum of MF dependence is shifted towards the higher magnetic fields range (from ca. 200 to 500 G) (see Fig. 2). Two important conclusions could be drawn on the basis of these findings. First, O_2 enters the reaction at the stage of MFE formation; second, in this case, MFE is formed in a biradical with different magnitude of effective exchange interaction. It is reasonable to suggest that these biradicals already contain oxygen. The most probable structure of these species corresponds to the adducts of O_2 with the biradicals **IV**, since the contribution of TPN resulting from T-biradical **IV** to the MFE grows in the presence of O_2. One can consider the formation of two types of oxygen containing paramagnetic species: oxygen-centered biradical (**V**) and the complex between **IV** and O_2 (**VI**):



V



VI



Scheme 5.

In addition to the above mentioned complexes of carbon-centered biradicals with oxygen [26,27], there are also experimental evidences of reversible formation of complexes between oxygen and the elements possessing vacant orbitals (transition metals) [29]. Unfortunately, at present it is impossible to decide between the structures **V** and **VI**.

The trend of the MFE field dependence observed in the presence of both O_2 and PPh_3 provides additional data on the interaction of biradicals with oxygen. In this case, the curve of MFE dependence is inverted relative to the that detected in the absence of PPh_3. The similarity of MFE dependencies (cf. Figs. 2 and 3) shows that the magnetic effect is also formed in the same oxygen-containing biradical, however, possessing an opposite multiplicity. Most probably, these species result from the interaction of O_2 with the complex **VII** (see Scheme 6). An ability of oxygen to substitute PPh_3, e.g. in iron complexes, has been described earlier [29]. The absence of magnetic field influence on the yield of TPN resulting from the complex **VII** could be related to small J values in the complex **VII**. Low magnitude of J does not allow the detection of the MFE within the studied range of external magnetic field strengths.

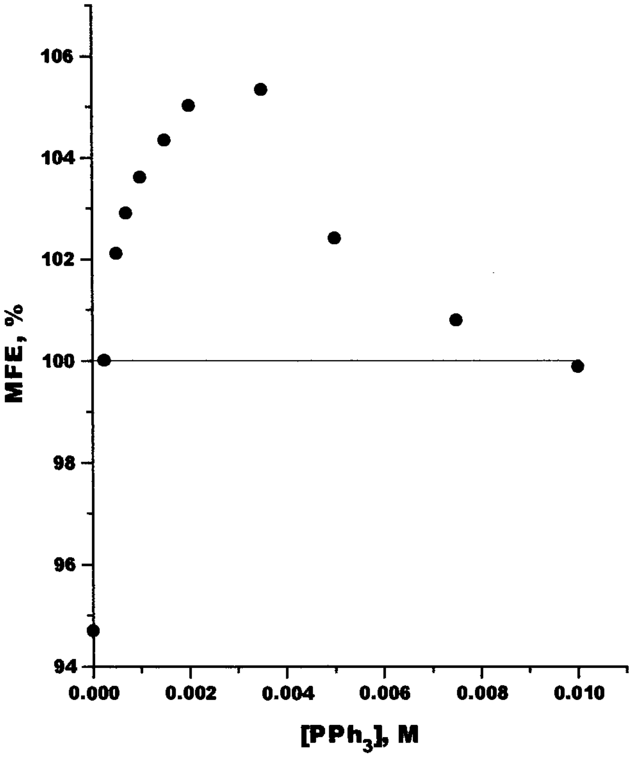
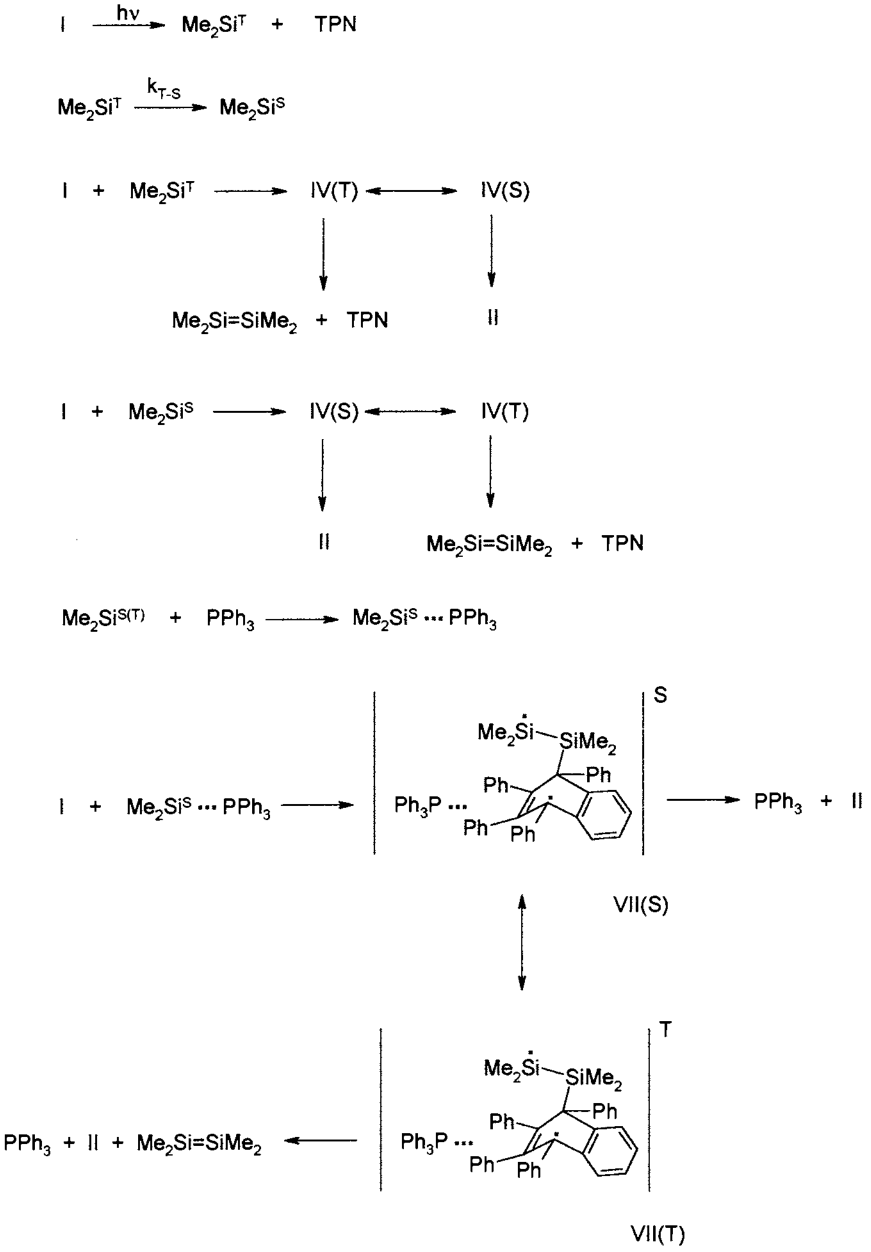


Fig. 6. The influence of Ph_3P concentration on MFE magnitude in the photolysis of **I** in aerated solutions (taken at the external magnetic field strength 550 G).

It also necessary to note that earlier observed [21] triplet–triplet quenching of the excited state of 7-germanorbornadiene by O_2 resulting in the decrease of the lifetime of corresponding triplet biradical analogous to **III** could be also MF sensitive. However, in the present case, the consideration of this process does not provide an explanation of the growth of MFE with the opposite signs.

4. Conclusions

Thus, the magnetic field effect detected in the photolysis of **I** in hexane solutions has confirmed the earlier conclusion on the involvement of paramagnetic intermediates (biradicals) in the process. The analysis of the trend of MFE field dependencies observed in the presence and in the absence of the scavengers of intermediate species (biradicals and dimethylsilylene) has allowed the identification of three independent precursors of the formation of the main stable reaction product, TPN. These are the biradicals **III**, **IV**, and complexes **VI** and **VII**. To explain the oxygen influence on the MFE magnitude, an assumption has been made about the existence of a complex between O_2 and biradicals **IV** (**V** or **VI**).



Scheme 6.

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