

## Attempts To Observe Spin Catalysis by Paramagnetic Particles in the Photolysis of 7-Silanorbornadiene in Solution

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Received: January 17, 2003

Addition of the stable radical, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-OH-TEMPO), to the reaction mixture in the photolysis of 7-silanorbornadiene in solution results in the decrease of the magnetic field effect detected for the yield of stable reaction product, tetraphenylanthracene (TPN). The dependence of TPN yield on 4-OH-TEMPO concentration obeys the Stern–Volmer equation; the estimated rate constant of the quenching of triplet dimethylsilylene by the stable radical is  $k_{\text{TEMPO}} = 1.4 \times 10^8 \text{ M}^{-1}$ . In accordance with the suggested hypothesis, the paramagnetic additives—the stable radical and  $\text{O}_2$ , which has been studied earlier—change the T–S conversion rate in the intermediate biradicals via the so-called spin catalysis mechanism.

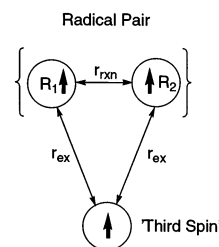
### Introduction

One of the most interesting problems of modern spin chemistry is the issue concerning the influence of nonzero spin species (stable radicals, biradicals, oxygen, etc.) on the rate and direction of radical reactions. In particular, active efforts are undertaken to investigate the variations of spin dynamics in the radical pairs (RPs), radical ion pairs (RIPs), or the biradicals under the influence of paramagnetic additive—so-called “third spin”.

This problem is of fundamental as well as of practical importance. First, the scope of the existing full theoretical description of the spin evolution covers only the radical pairs with half-integer total electron spin of both partners. On the other hand, a great number of experimental systems where the singlet–triplet evolution involves paramagnetic particles with more complex electronic structure than simple hydrocarbon radicals with the electron spin  $S = 1/2$  could be found in the literature. This specifically applies to the biologically relevant processes.<sup>1</sup> In particular, one should note a number of processes of enzymatic oxidation by heme-containing enzymes such as horseradish peroxidase and cytochromes also involving so-called multispin systems.<sup>2</sup> In these processes, the electronic structure of the iron atom of the reactive intermediates includes both low- and high-spin states.<sup>3</sup> Analysis of magnetic field effects detected in these systems in the framework of RP theory could not take into account the presence of other electrons of the RP partners (see, e.g., studies of the influence of magnetic field on the enzymatic oxidations mediated by horseradish peroxidase<sup>2</sup>).

Substantial contribution to the modern understanding of the influence of paramagnetic particles on the spin evolution in RPs has been made by Buchachenko and Turro and co-workers. In 1994, they found that the presence of paramagnetic particles accelerates the rate of singlet–triplet conversion in the radical reactions and increases the probability of the RP recombination.<sup>4</sup>

### SCHEME 1: Schematic Presentation of the Influence of a Stable Radical on the Spin Evolution in a Radical Pair<sup>a</sup>



<sup>a</sup>  $r_{\text{ex}}$  is the contact radius of the electron exchange interaction with the third spin;  $r_{\text{rxn}}$  is the reaction radius of the radicals  $R_1$  and  $R_2$ .

The phenomenon was referred to as “spin catalysis”.<sup>4</sup> At present, two mechanisms of the influence of the third spin on the spin evolution in RPs, RIPs, and biradicals have been discussed. The basis for the first proposed mechanism of the T–S conversion in the RPs under the influence of paramagnetic species is nonmagnetic interaction—spin exchange between the electron spins of the RP partners and the electron spin of the catalyst (“third spin”).<sup>5</sup> The second mechanism considers the influence of dipole–dipole interaction, which increases the population of a singlet reactive state of RPs or biradicals through the mixing of S with  $T_+$ ,  $T_0$ , and  $T_-$  levels.<sup>6</sup> The influence of stable radicals, which are highly reactive trapping agents of the short-lived radicals, on the spin evolution is believed to be possible due to the difference in the contact radii of the electron exchange interactions  $J$  of the unpaired electrons of the stable radical and those of the RP partners or biradicals ( $r_{\text{ex}} \sim 12 \text{ nm}$ ), and the distance at which the reactions/recombination occurred ( $r_{\text{rxn}} \sim 2r_0$ , where  $r_0$  is a contact radius of the RP radicals) (see also Scheme 1).<sup>7</sup> This conclusion has recently received additional confirmation when the influence of a stable radical on CIDNP effects formed in the RPs of short-lived radicals has been observed.<sup>8</sup>

Selected papers were devoted to the investigations of the processes of CIDEP transfer between two sorts of paramagnetic particles—stable radicals and triplet and doublet excited states.<sup>9,10</sup> In fact, these papers were the first to demonstrate the effect of

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the electron spin exchange between the stable radical and the short-lived one.

Some recent publications also discuss the results of the investigations of magnetic field effects in multispin systems.<sup>11–14</sup> Unlike the papers on spin catalysis, the majority of these investigations involve systems where the stable radicals are bound to one of the reagents and influence the spin evolution via the electron–dipole interaction. The systems with stable radicals bound to one of the reagents are of special interest from the chemical viewpoint. From our perspective, these systems might be of interest from the viewpoint of the potentiality of the stable radicals and biradicals—commonly used as paramagnetic scavengers—to form complexes with the reagents of the radical reactions. It is necessary to emphasize that the formation of weak (the dissociation energy of the chemical bond being about several kilocalories) donor–acceptor  $\pi$ – $\pi$ ,  $\pi$ – $\sigma$ , and  $n$ – $\pi$  complexes between the paramagnetic particles, such as stable radicals and oxygen, and a number of diamagnetic compounds is a well-known fact.<sup>15</sup> There are also certain evidences of the influence of similar complexation on the parameters of chemical reactions.<sup>11,14</sup> Thus, one cannot exclude that, in the systems where RP partners are not chemically bounded to the stable radicals/biradicals, the influence of the third spin could manifest itself via complexation. Although it is still not clear whether the interactions of the paramagnetic species in these complexes are a manifestation of the spin catalysis, it is necessary to stress that the effects of the third spin were observed only for a limited number of the experimental systems. Therefore, new experimental evidences of the influence of paramagnetic species on the radical reactions should provide the answer to the above-mentioned question. The exploration of the chemical manifestations of selected types of the interactions inherent in some paramagnetic particles, in particular spin catalysis, and in real chemical processes is believed to be a very prospective field of research.

Some reference data also point to the potential complexation between two paramagnetic species—oxygen and short-lived biradicals.<sup>13,16</sup> It was suggested<sup>16</sup> that the intermediate biradicals generated through the photolysis of aromatic ketones via the Norrish Type II mechanism could reversibly form weak complexes with molecular oxygen. This conclusion was based on the effect of oxygen on the biradical lifetime as well as on the yield of the reaction products. Another example is the influence of O<sub>2</sub> on the magnitude of the magnetic field effect (MFE) on the yield of products in the photolysis of 7-silanorbornadiene in solution.<sup>13</sup> The reaction mechanism proposed on the basis of laser pulse photolysis experiments and the analyses of CIDNP effects and the MFE suggests that the observed MFE is formed in short-lived silicon-centered 1,6-biradicals. In the presence of equilibrium concentration of the dissolved oxygen, the MFE demonstrates a more than 2-fold increase as compared to the case of the deaerated solutions, and the maximum of the MFE dependence on the external magnetic field strength shifts toward the higher field region. According to the radical pair theory, such a shift of the extreme suggests that in aerated and deaerated solutions the MFE is generated in the paramagnetic intermediates of different structure. In the aerated solutions this shift has been attributed to the complex of the 1,6-biradical with O<sub>2</sub>.<sup>13</sup> To check the hypothesis about the complexation of two paramagnetic particles and to explore whether the influence of oxygen could be regarded as an example of spin catalysis, it would be reasonable to investigate the influence of other paramagnetic species on the photolytic decomposition of 7-silanorbornadiene. To this end, in the present paper we have

studied the photodecomposition of 7-silanorbornadiene in the presence of the stable radical in the magnetic fields of different strengths, by means of laser pulse photolysis.

## Experimental Section

The laser pulse photolysis technique was used to study the photodecomposition of the solutions of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**1**) ( $(0.9–1.0) \times 10^{-3}$  M in hexane) in the presence and in the absence of stable 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl radical (4-OH-TEMPO), in aerated and deaerated solutions. 4-OH-TEMPO was a kind gift from Prof. I. A. Grigoriev (Novosibirsk Institute of Organic Chemistry) and was recrystallized prior to all experiments. Hexane (JSC Mosreaktiv) was purified by distillation. The samples were photolyzed with an excimer (XeCl) laser:  $\lambda = 308$  nm, pulse duration 15 ns, average pulse energy ca. 10 mJ, delay time 50 ns. The detailed description of the setup could be found elsewhere.<sup>17</sup> The concentration of 4-OH-TEMPO was varied in the range  $(0.2–1.5) \times 10^{-2}$  M. According to reference data,<sup>18</sup> in aerated solution in hexane, the equilibrium oxygen concentration amounts to  $2 \times 10^{-3}$  M. To prepare the deaerated solution, the samples were purged by the argon flow for 15 min to displace the dissolved oxygen. All experiments were performed at ambient temperature and at atmospheric pressure.

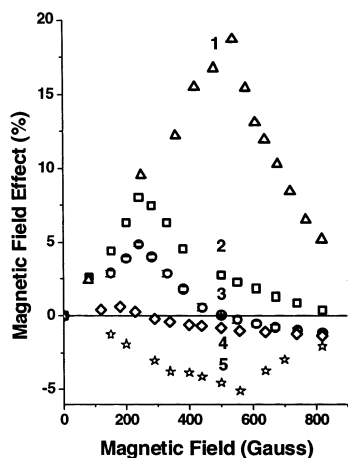
The external magnetic field was created by the permanent Sm–Co magnet with one sliding pole to ensure the variation of the magnetic field strength. The magnetic field effect was monitored by the level of optical absorption of the end photolysis product—tetraphenyl-naphthalene (TPN). As has been shown earlier,<sup>19</sup> the change in the optical density of the solution of **1** after the laser pulse ( $\Delta D$  at  $\lambda = 334$  nm) is determined by the optical absorption of the resulting TPN. The MFE was calculated according to the formula

$$\text{MFE} = [(\Delta D - \Delta D_{\text{H}})/\Delta D] \times 100\%$$

where  $\Delta D$  ( $\Delta D_{\text{H}}$ ) is the absorption change detected under the geomagnetic (external) field, respectively. Data points of the MFE dependencies show the results of standard statistical processing of seven to nine kinetic traces taken in laser pulse photolysis experiments during the photodecomposition of **1**. The error bars represent the standard deviation.

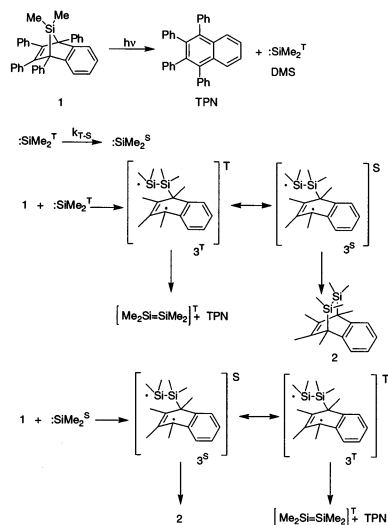
## Results and Discussion

The scheme of the photodecomposition of 7-silanorbornadiene (**1**) in solution has been formulated earlier<sup>13,14</sup> on the basis of the laser pulse photolysis data and from the analysis of CIDNP and the MFE observed in this reaction (see Scheme 2). According to this scheme, the magnetosensitive stage responsible for the formation of the MFE is the singlet–triplet conversion in 1,6-biradicals (**3**) formed through the reaction of the initial **1** with the dimethylsilylene Me<sub>2</sub>Si: (DMS) in triplet excited and singlet ground states. Since the sign of the observed MFE is dependent on the multiplicity of the starting 1,6-biradical (**3<sup>T</sup>** or **3<sup>S</sup>**, respectively; see Scheme 2), it will be stipulated by the ratio of the reaction rates of initial **1** with the T- and S-states of DMS and the rate of its triplet to singlet conversion,  $k_{\text{T} \rightarrow \text{S}}$ . It has been shown that in the absence of quenchers and in the presence of oxygen the contribution of the reaction of triplet excited DMS becomes prevalent, while in the presence of the diamagnetic scavengers of DMS—triphenylphosphine (Ph<sub>3</sub>P) and carbon tetrachloride (CCl<sub>4</sub>)—we have observed the changes in magnitude and the alteration of the sign of the MFE.<sup>13,20</sup> This



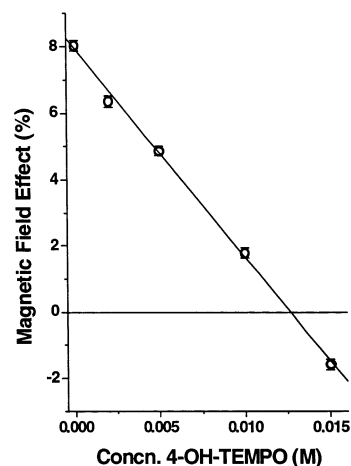
**Figure 1.** Magnetic field effects in the photolysis of 7-silanorbornadiene (**1**) ( $1 \times 10^{-3}$  M solution): in the aerated solution (1,  $\Delta$ ); deaerated, in the absence of any scavengers (2,  $\square$ ); deaerated, in the presence of 4-OH-TEMPO ( $5 \times 10^{-3}$  M solution) (3,  $\circ$ ); deaerated, in the presence of triphenylphosphine ( $\text{Ph}_3\text{P}$ ) ( $2 \times 10^{-3}$  M solution) (4,  $\diamond$ ); aerated, in the presence of  $\text{Ph}_3\text{P}$  ( $2 \times 10^{-3}$  M solution) (5,  $\star$ ).

### SCHEME 2: Photolysis of 7-Silanorbornadiene (**1**) in Solution



observation suggests in the presence of the scavengers the reaction of the singlet state of DMS is prevalent. Figure 1 shows the magnetic field dependencies of the MFE detected in earlier papers<sup>13,19</sup> as well as those observed in this work in the presence of several different scavengers (1, 3–5, see Figure 1). For comparison, the same figure shows the field dependence of the MFE detected in the absence of any scavengers (2, see Figure 1). Field dependence (3) was measured in the presence of a 5-fold excess of 4-OH-TEMPO (Figure 1). It is evident from the comparison of the dependencies (1 and 3) with the effect observed in the absence of the scavengers (2) that the influence of a stable radical on the MFE differs from that of  $\text{O}_2$ : the decrease of the MFE is observed instead of the increase, and the extreme point of the field dependence does not change its location.

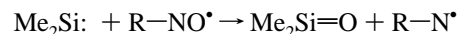
To clarify the mechanism of the influence of a stable radical on the process under study, the dependencies of the MFE magnitude and TPN yield on the concentration of 4-OH-TEMPO were measured. The dependence of the MFE magnitude on the concentration of 4-OH-TEMPO was studied at the magnetic field strength  $H = 240$  G, which corresponds to the MFE maximum of the magnetic field dependence in the absence of



**Figure 2.** Dependence of the magnetic field effect detected in the photolysis of 7-silanorbornadiene (**1**) ( $1 \times 10^{-3}$  M solution) on the 4-hydroxy-TEMPO concentration in deaerated solution at the magnetic field strength  $H = 240$  G.

scavengers (2, Figure 1). With the growth of the stable radical concentration, the MFE decreases monotonically (Figure 2), and in the region of the highest possible concentrations of 4-OH-TEMPO, the alteration of the MFE sign is observed. As has been mentioned above, the opposite sign of the MFE points to the prevalent contribution from the singlet paramagnetic precursor of TPN—one might suggest that this precursor is the 1,6-biradical  $3^S$  in the initial singlet state (Scheme 2). Thus, in the region of high concentrations of 4-OH-TEMPO, the initial 7-silanorbornadiene (**1**) predominantly reacts with the DMS in the ground singlet state.

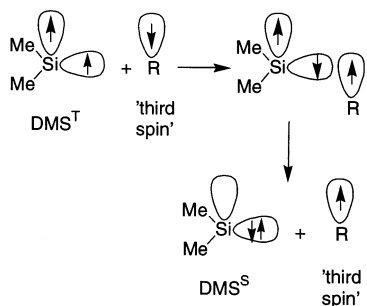
According to the reference data on the reactivities of carbenes with the stable nitroxyl radicals,<sup>9</sup> one might suggest that DMS reacts with 4-OH-TEMPO to form dimethylsilylone:



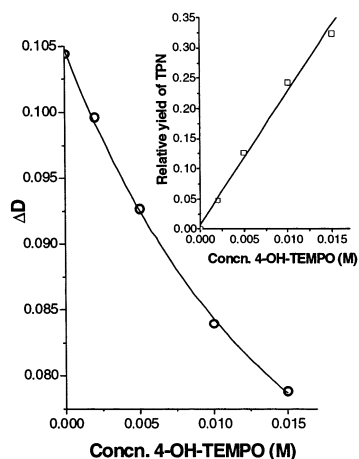
Unfortunately, we were unable to detect this reaction, since silanone is extremely unstable, and during the photolysis it would be converted to siloxane oligomers, which, in fact, are among the products of the photolysis of **1** in the experiment without stable radicals, too.<sup>19</sup> However, the alteration of the MFE sign in the region of high concentrations of the stable nitroxyl radical (see Figure 2) shows that DMS has not undergone irreversible transformation; instead, the increased concentration of 4-OH-TEMPO causes T–S conversion of  $:\text{SiMe}_2^{\text{T}}$  to  $:\text{SiMe}_2^{\text{S}}$ .

The acceleration of T–S conversion of the carbene analogue induced by the presence of nitroxyl radical could result from the interaction of these two paramagnetic species. In fact, the excited triplet state of DMS could be regarded as a biradical with two unpaired electrons belonging to the single silicon atom. Consequently, the acceleration of the T–S conversion of DMS in the presence of the “third spin” (4-OH-TEMPO) could be regarded as a manifestation of the spin catalysis. The reversal of the spin orientation of DMS is mediated by an electron exchange interaction of its two spins and that of the stable radical. According to predictions made by Buchachenko and Berdinsky,<sup>6</sup> the electron exchange interaction of the “spin catalyst” and the partners of the RP could induce the reorientation of their spins and convert the triplet state of the RP to the singlet one. The variation of the total spin resulting from this transformation is compensated by the change of the spin of the “catalyst”, that is, the stable radical. The process of the triplet





**Figure 3.** Schematic presentation of T–S conversion of  $:\text{SiMe}_2$  induced by the presence of a stable radical.



**Figure 4.** Dependence of the yield of TPN in the photolysis of **1** ( $9 \times 10^{-4}$  M solution) on 4-OH-TEMPO concentration in deaerated solution. The inset shows the Stern–Volmer plot.

to singlet conversion of DMS in the presence of the stable radical (“third spin”) is schematically shown in Figure 3.

The dependence of the yield of TPN on the concentration of 4-OH-TEMPO has also been analyzed (see Figure 4). The slope  $k\tau$  of the Stern–Volmer plot presented in the inset in Figure 4 is equal to  $22 \text{ M}^{-1}$ . Using the earlier estimate of the lifetime of triplet DMS ( $\tau \leq 1.4 \times 10^{-7} \text{ s}$ ),<sup>13</sup> one could obtain the reaction rate constant of the interaction of DMS and 4-OH-TEMPO,  $k_{\text{TEMPO}} = 1.6 \times 10^8 \text{ M}^{-1} \text{ c}^{-1}$ . On the other hand, the rate constant of the reaction of DMS with the initial 7-silanorbornadiene (**1**) was shown to be equal to  $k_1 = 5.7 \times 10^9 \text{ M}^{-1} \text{ c}^{-1}$ .<sup>19</sup> As was mentioned above, this reaction is crucial for the formation of the MFE in the photolysis of 7-silanorbornadiene (**1**) (see Scheme 2). Thus, the comparison of the rate constants of the two above-mentioned reactions— $k_{\text{TEMPO}}$  and  $k_1$ —shows that the initial **1** might successfully compete with 4-OH-TEMPO in the reaction with DMS. The manifestation of the MFE of both signs depending on the concentration of 4-OH-TEMPO (Figure 4) confirms that such competition does take place.

In summary, the above results of the performed experiments show that two paramagnetic additives—stable radical 4-OH-TEMPO and oxygen—have different effects on the MFE detected in the photolysis of **1**. It is possible to formulate the following conclusions.

It is reliably established that the stable radical under study, 4-OH-TEMPO, reacts predominantly with DMS (not with the 1,6-biradical **3**; see Scheme 2). The absence of the shift of the magnetic field dependence (the identical location of the extremes of the dependences 2 and 3 in Figure 1) implies no complexation between the biradical **3** and 4-OH-TEMPO, in contrast to the reaction in the aerated solutions, where the formation of the complexes of **3** and  $\text{O}_2$  has been suggested.<sup>13</sup> From our

viewpoint, the manifestation of different patterns of the magnetic field dependences of the MFE detected in the presence of  $\text{O}_2$  or 4-OH-TEMPO is confirmed by the suggestions on complexation of  $\text{O}_2$  with the 1,6-biradicals **3**. One might suggest several feasible structures of this complex—these might include a  $\pi$ -complex formed through the interaction between  $p$ -orbitals of  $\text{O}_2$  and the naphthalenic structural element of the 1,6-biradical **3**; otherwise, it might result from donor–acceptor interaction between the lone electron pair of  $\text{O}_2$  and empty  $d$ -orbitals of silicon atom postulated in the literature.<sup>21</sup> It should be noted that the reference data<sup>15</sup> also provide similar examples of the complexation between  $\text{O}_2$  and a number of diamagnetic aromatic and organosilicon compounds.

In conclusion, it is expedient to raise a point whether one might consider the effect of oxygen on the MFE in the 1,6-biradicals to be a manifestation of spin catalysis. In our opinion, this possibility is determined by following two criteria characterizing the spin catalysis phenomenon. In accordance with the present understanding,<sup>4,5</sup> a paramagnetic additive playing the role of a “spin catalyst” does not enter the reaction but instead should increase the recombination probability of a radical pair or biradical. A possible mechanism involves magnetic field-insensitive interaction, namely, the spin exchange between the spins of the RP partners and that of the catalyst, resulting in the T–S conversion of the RP and, therefore, the change of the MFE magnitude.

As has been shown,<sup>13</sup> the photolysis of **1** in aerated solutions does not result in the formation of any new reaction product generated due to the presence of oxygen but demonstrates a significant increase of the MFE magnitude (cf. the dependences 1 and 2, Figure 1). From the viewpoint of the above criteria, one might conclude that, in the photolysis of **1** in aerated solution,  $\text{O}_2$ , indeed, plays a role of “spin catalyst”, promoting the product formation. In this process, the electron exchange interaction between oxygen and the unpaired electrons of the biradical is capable of inducing the triplet–singlet conversion between the  $T_+$ ,  $T_0$ ,  $T_-$ , and  $S$  levels of the biradical in the external magnetic field. It is essential that within the scope of this mechanism one should expect the increase of the MFE of both signs, which is clearly seen from the experimental results (cf. 1 and 2, 4 and 5, respectively, Figure 1). From Scheme 2, it is evident that, in the case of the predominance of the triplet biradicals  $\mathbf{3}^T$ , oxygen increases the probability of their T–S conversion to singlet biradicals  $\mathbf{3}^S$ , thus decreasing the yield of TPN (formed from the triplet biradical  $\mathbf{3}^T$ ). This results in the increase of the positive MFE (cf. the dependences 1 and 2, Figure 1). On the other hand, due to the spin catalysis, the interaction of oxygen with the singlet 1,6-biradical  $\mathbf{3}^S$  should increase the probability of its S–T conversion to the triplet state  $\mathbf{3}^T$ , leading to the growth of the yield of TPN. In the frames of the proposed model, this corresponds to the increase of the negative MFE (cf. the dependences 4 and 5, Figure 1).

It is also necessary to mention that the conclusion on the manifestations of the spin catalysis induced by paramagnetic species chemically bound to the reacting radicals is consistent with the data on the MFE observed in the reactions of single electron transfer.<sup>11,12</sup> In these processes the greatest MFEs were observed if a stable radical was chemically bound to one of the RIP’s partners. While free stable radicals in the bulk have not shown any noticeable effect on the escape of the radicals from a micelle,<sup>12</sup> on the other hand, the analysis of the third spin effect on the recombination probability<sup>6</sup> and on CIDNP effects formed in the RPs in nonviscous solutions<sup>8</sup> does not give any grounds to suggest the complexation between the stable radical

and RP partners. The comparison of the results of the MFE study of the photolysis of 7-silanorbornadiene (**1**) in the presence of a stable radical and findings observed when the MFE was studied in the photolysis of **1** in the presence of various quenchers<sup>14</sup> with the reference data on the spin catalysis<sup>4</sup> and MFEs in micelles<sup>12</sup> and in radical ion reactions<sup>11</sup> points to the different peculiarities of the influence of paramagnetic species on the spin evolution in the RP of free radicals in nonviscous solution, in the radicals formed in micelles, as well as in radical ion pairs. Apparently, these distinctions stem from the different molecular dynamics characteristic for the above-mentioned systems and, in particular, stipulated by the role of the long trajectories of the motion of partner radicals before the recombination. This conclusion is confirmed by the investigation of the influence of stable radicals on CIDNP effects.<sup>8</sup> Undoubtedly, in the case of radical ion pairs, the contribution of the long trajectories to recombination is lower as compared to the case of neutral free radicals.<sup>22</sup> It is reasonable to suggest that the peculiarities of micellar systems demonstrating low MFEs are closer to those of the particles with limited diffusion and are markedly different from the behavior of free radicals in nonviscous solutions. Unfortunately, the literature lacks data on the peculiarities of the molecular motion of the biradicals studied in the present paper. Since the complexation of two paramagnetic particles (e.g., O<sub>2</sub> and 1,6-biradical) is suggested to be prerequisite of the effective influence on their spin evolution, one might assume that 1,6-biradicals (**3**) should demonstrate certain rigidity.

**Acknowledgment.** The authors thank the Russian Foundation for Basic Research (RFBR) and INTAS (RFBR Project No. 00-03-33048 and INTAS-RFBR Cooperative Project No. 97-03-71065) and the Russian Federal Special Scientific and Technological Program for the Research and Development of Prioritized Trends in Science and Technology (Highly Reactive Intermediates of Chemical Reactions, No. 41.002.11.1402) for their financial support. We also thank Prof. I. A. Grigoriev (Novosibirsk Institute of Organic Chemistry) for the gift of 4-OH-TEMPO.

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