

Paramagnetic intermediates in the photoinduced reaction between dodecamethylcyclohexasilane and 9,10-phenanthraquinone: Time-resolved CIDNP study

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Abstract

The reaction between dodecamethylcyclohexasilane (Me_2Si)₆ **1** and 9,10-phenanthraquinone **2** has been studied by means of CIDNP method. In the polar solvent, the photodecomposition of **1** is shown to proceed via triplet radical ion pair formed by phenanthraquinone radical anion and cyclohexasilane radical cation. Its transformation leads to the cyclic reaction product – 10-membered cyclic dioxahexasilene **8** – formally resulting from the addition of linear 1,6-silicon-centered biradical $\cdot\text{Si}(\text{Me})_2\text{-Si}_4(\text{Me}_2)_4\text{-(Me)}_2\text{Si}\cdot$ to C=O bonds of quinone. Product **8** is unstable, after several hours it converts to dioxasilole **4** via sequential repeated elimination of dimethylsilylenes **3**. © 2005 Elsevier B.V. All rights reserved.

Keywords: Dodecamethylcyclohexasilane; 9,10-Phenanthraquinone; CIDNP; Photoinduced electron transfer; Radical ion pair

1. Introduction

Processes involving the intermediate step of single electron transfer are of special interest in the organosilicon chemistry. In recent decades, many research groups have explored this area, and a vast pool of the experimental data obtained have been summarized and analyzed in the detailed results with the discussion of the possible investigation prospects (see, e.g., [1–4]). Different methods used to generate and to investigate short-lived silicon-centered radical cations and radical anions include ESR [5], cyclic voltammetry [6], preparative electrolysis [7], electron impact [8], γ -irradiation [9], photolysis in highly polar media [10], etc.

Nevertheless, despite the undoubted interest and great number of publications on the transformation of organosilicon compounds generated through single electron transfer, there are only several examples of processes where the

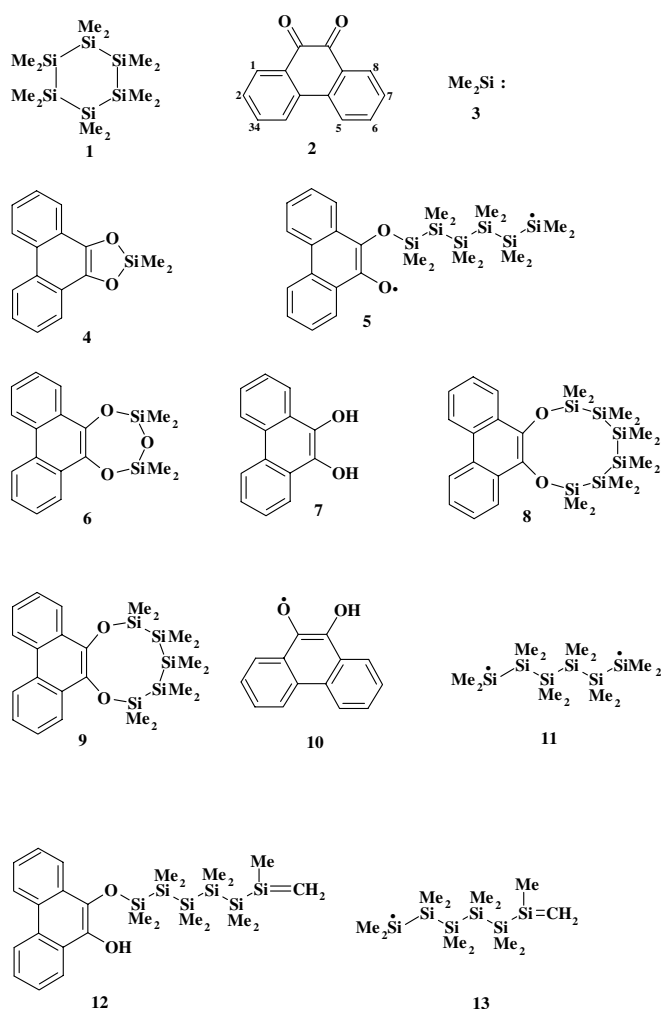
paramagnetic intermediates have been detected by physical methods [11]. However, high sensitivity and accuracy of structural identification of short-lived particles by spin chemistry methods – Chemically Induced Dynamic Nuclear Polarization (CIDNP), Chemically Induced Dynamic Electron Polarization (CIDEP), and Magnetic Field Effects (MFE) – make them extremely useful for the investigation of structure and reactivity of organometallic paramagnetic intermediates. Numerous examples demonstrate the successful application of these methods to the investigations of organometallic reactions involving Si- and Ge-derivatives [12–17].

The present paper is devoted to the investigation of paramagnetic intermediates in the photoinduced interaction between dodecamethylcyclohexasilane **1** and 9,10-phenanthraquinone **2** under the conditions favouring the formation of radical ions – e.g., media of high polarity – by means of ¹H CIDNP method. Photoinduced reactions of cyclic oligosilanes and quinone **2** have been earlier studied in the polar and nonpolar media – acetonitrile

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and benzene [18]. In both solvents, the formation of 2,2'-dimethylphenanthro[9,10-d][1,3,2]dioxasilole **4** has been observed – formal product of the transfer reaction of dimethylsilylene Me_2Si : **3**. It was assumed [18] that the first step of the photoinitiated reaction in both polar and nonpolar media is the triplet excitation of quinone **2**. In polar medium, this is followed by single electron transfer from oligosilane to quinone resulting in radical ion pair (RIP). It was further suggested, thereafter, that interaction of the electric charges accompanied by the ring opening of cyclic silane leads to biradical **5** [18]. Further transformation of **5**, namely the elimination of the silyl biradical chained fragments, results in the end reaction product **4** together with the minor product 2,2',4,4'-tetramethylphenanthro[9,10-f][1,3,5,2,4]trioxadisilole **6** (see Scheme 1).



However, the investigations described in [18] gave no unambiguous evidences of the formation of radical cation of cyclic silane. This uncertainty as well as the lack of data on the structures of short-lived intermediates of the final products of the reaction under study have stimulated our attempt to revisit the photoinduced interaction of **1** and **2** by means of ^1H CIDNP to elucidate the structures of paramagnetic intermediates of the process.

2. Experimental

The photolysis of reaction mixture of **1** and **2** was carried out directly in the probe of NMR spectrometers. Saturated solution of dodecamethylcyclohexasilane **1** in commercial deuteroacetonitrile (CIL) was used (molar concentration of **1** was $\geq 10^{-3}$ M), the concentration of 9,10-phenanthraquinone **2** was varied in the range from 5×10^{-3} to 5×10^{-2} M. All experiments were performed at ambient temperature. The reaction mixtures were deaerated by 30 min of Ar bubbling prior to irradiation. Dodecamethylcyclohexasilane **1** has no absorption in the wavelength region >300 nm, therefore under the present conditions the direct photolysis of **1** does not take place.

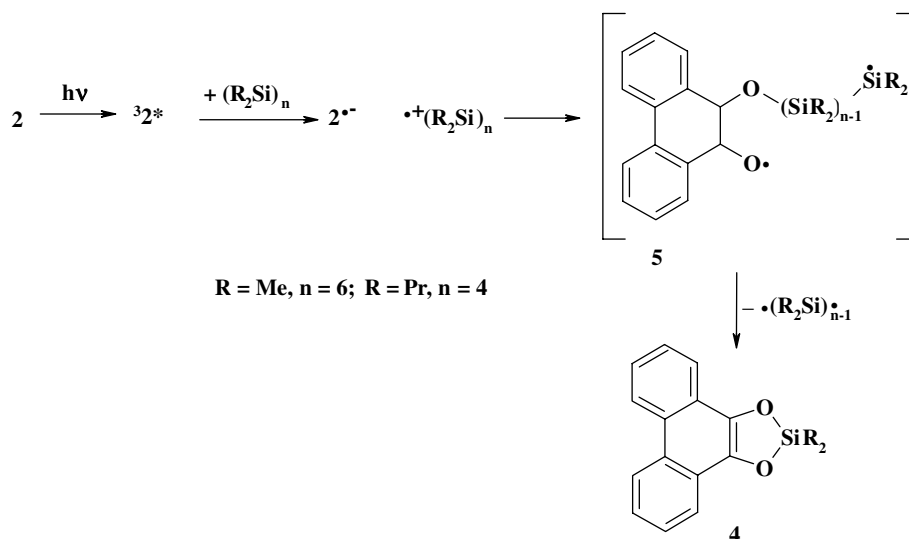
NMR spectra were taken using JEOL JNM FX90Q (^1H operating frequency 90 MHz) equipped with a photochemical device for sample irradiation by the thermal filtered light of high pressure mercury lamp (DRSh-1000, 1 kW power). In time-resolved CIDNP experiments, the samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of Bruker DPX 200 NMR spectrometer (^1H operating frequency 200 MHz). To initiate the photochemical reaction, in this case, EMG 101 MSC Lambda Physik excimer laser ($\lambda = 308$ nm, pulse duration 15 ns, average pulse energy 100 mJ) was used. In the time resolved (TR) CIDNP experiments, we have used standard presaturation technique to suppress the equilibrium signals involving the sequence: (i) saturating radio-frequency pulse; (ii) laser pulse; (iii) time delay; (iv) detecting radio-frequency pulse; (v) free induction decay. In the TR CIDNP experiments, 2 μs detecting radio-frequency pulse was used. Quasi Steady State (QSS) CIDNP experiments were performed using the special presaturation technique: saturation -180° pulse – a train of laser pulses – evolution time – detection pulse – free induction decay. Since the background (equilibrium) NMR signals in CIDNP spectrum were suppressed, only the signals of the substances demonstrating nuclear polarization could be observed.

The analysis of CIDNP effects in radical ion reactions was carried out in accordance with empirical rules [19]. The magnetic properties of the paramagnetic intermediates formed in the reaction under study necessary for the analysis of ^1H CIDNP effects are shown in Table 1.

GS/MS analysis of the irradiated reaction mixture was carried out by means of Agilent Technologies HP6890N/HP5973N mass-spectrometer using the capillary columns HP-5MS with step-gradient heating from 50 to 150 $^\circ\text{C}$.

3. Results and discussion

Fig. 1 shows the NMR spectra taken during the photolysis of **1** and **2** in CD_3CN by mercury lamp. It is seen from Fig. 1 that after 300 s of photolysis, two new NMR signals are observed in the characteristic region of methyl protons at Si-atoms, δ 0.33 ppm (s), and 0.06 ppm (s), while the downfield region shows the lines of hydroquinone **7**. However, after the reaction mixture was kept for several hours



Scheme 1. The mechanism of photoinduced reaction between oligosilanes and phenanthraquinone in the polar medium [18].

Table 1
Magnetic properties of the paramagnetic intermediates [24]

Paramagnetic intermediate	<i>g</i> -Factor	Hyperfine interaction (mT)
<p style="text-align: center;">(1+•)</p>	2.0093	0.282 (18H) 0.094 (18H)
<p style="text-align: center;">(2•-)</p>	2.0048	-0.158 2H(1,8) +0.034 2H(2,7) -0.173 2H(3,6) +0.041 2H(4,5)

at ambient temperature, the high field portion of NMR spectrum changes, and the signal of the main product appears at δ 0.36 ppm (s) (Fig. 1(c)). This behavior indicates that in contrast to the conclusions of [18], possible structures of the reaction products are not that straightforward and require special consideration. Primary product detected immediately after the photolysis has the chemical shift δ 0.33 ppm (Fig. 1(b)), and it seems unlikely that this signal could be attributed to dioxasilole **4**, since according to data of [18], the latter is stable under ambient conditions. While the NMR signal at δ 0.33 ppm disappears after the reaction mixture was kept at ambient temperature during 4–5 h, this process is accompanied by the manifestation of the new lines in the NMR spectra after reaction (δ 0.09 ppm (s) and 0.36 ppm (s)) (Fig. 1(c)).

The structures of these reaction products have been determined by means of GC/MS analysis of the reaction mixture immediately after UV irradiation and compared to the results observed after the irradiated samples were

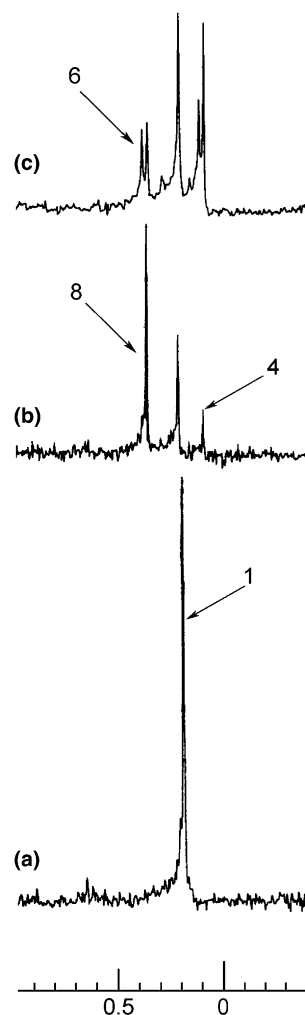


Fig. 1. 90 MHz ^1H NMR spectra (aliphatic portion) of the reaction mixture of dodecamethylcyclohexasilane **1** and 9,10-phenanthraquinone **2** in CD_3CN : (a) prior to photolysis; (b) after 5 min of UV irradiation by mercury lamp; (c) after ca. 3 h of sample storage at ambient temperature (8 scans).

kept under ambient temperature during several hours. GC/MS analysis of the reaction mixture immediately after the photolysis shows the presence of the product with molecular ion of m/z 556 (m/z (%): 556(M^+ , 2), 541(5), 309(5), 290(29), 266(100), 236(6), 217(7), 189(5), 159(8), 131(16), 73(40)). This corresponds to the product of the addition of initial cyclohexasilane **1** to quinone **2** resulting in the formation of 2,2',3,3',4,4',5,5',6,6',7,7'-dodecamethylphenanthro[9,10-i][1,8,2,3,4,5,6,7] dioxahexasilicine **8** (δ 0.33 ppm) – 10-membered ring cyclic molecule. Dioxahexasilicine **8** was found to be thermally unstable, it readily decomposes at room temperature. Indeed, after the irradiated sample was kept under ambient conditions during several hours, the GC/MS spectra lack the product with the molecular ion of m/z 556. In this case, the highest molecular mass peak was for molecular ion of m/z 498 (m/z (%): 498(M^+ , 23), 483(28), 425(5), 351(7), 293(17), 266(100), 232(33), 174(33), 143(8), 116(40), 73(70)). Based on the fragmentation pattern, we have suggested that the latter product is 9-membered cyclic 2,2',3,3',4,4',5,5',6,6'-decamethylphenanthro[9,10-h][1,7,2,3,4,5,6] dioxapentasilicine **9**. However, **9** was also found to be unstable; one day after the reaction mixture was kept at room temperature, it was not observed in the GC/MS spectra. To our knowledge, the formation of **8** and **9** was not earlier described in the literature. Both products were not detected in earlier studies of the photoinduced interaction of **1** and **2** [18], even in the reaction in polar media (CH_3CN/CH_2Cl_2). This discrepancy between our results and the reference data seems to be due to the different photolysis conditions: different sources of UV irradiation in our experiments and the irradiation time that was appreciably shorter (minutes) as compared to that in [18] (hours), so the contribution from the secondary photolysis would be smaller. Another possible explanation of the observed discrepancy could be the partial decomposition of **8** and **9** before/during GS/MS analysis. One should also mention that the formation of **8** was not observed after the photolysis of **1** and **2** in benzene. In all analyses, together with **8** and **9** peaks with m/z 266 and 360 were observed corresponding to dioxasilole **4** (δ 0.06 ppm), and trioxadisilicine **6** (δ 0.36 ppm). However, under the present reaction conditions, the ratio **4/6** differs from that reported in [18].

To clarify the mechanism of the product formation, we have explored 1H CIDNP effects generated under the irradiation of the excimer laser. One should point out that excitation by laser does not alter the set of the reaction products as compared to that observed under the irradiation by mercury lamp (see Fig. 1). Fig. 2 shows QSS spectra taken during the photolysis of **1** and **2** in CD_3CN . Spectra show CIDNP effects of the initial phenanthraquinone **2** and the reaction products – hydroquinone **7** and dioxahexasilicine **8**. All the above effects were observed only if the photolyses were carried out in polar medium, i.e., in deuterioacetonitrile. This allows us to make several preliminary conclusions pertaining to the reaction mechanism.

First, the generation of CIDNP effects appearing only in polar solvent with simultaneous CIDNP formation of the initial compound is characteristic for single electron transfer process (SET) [20]. Moreover, the possibility of SET reaction between **1** and **2** was also confirmed by the analysis performed in [18] in accordance with well-known Rehm–Weller criterion.

The analysis of CIDNP effects of quinone **2** (emission (E) of the protons in (1,8)- and (3,6)-positions and enhanced absorption (A) of the protons in (2,7)- and (4,5)-positions) according to Kaptein's rules [19] leads to the conclusion about the formation of triplet radical ion pair ($E = \mu(+)\times\epsilon(+)\times\Delta g(-)\times HFI(-)\times\gamma(-)$) (RIP-1, see Scheme 2). Indeed, it is well-known that the quinone **2** is absorbing the light quantum followed by rapid conversion to the triplet excited state ($E_T \sim 48$, $E_S \sim 54$ kcal/mol) [21] which is reactive towards **1**. The sign of γ points out that the back electron transfer resulting in the quinone recovery occurs from triplet RIP, too. This might be possible because the RIP energy levels and triplet energy E_T levels of **2** are very close to each other. According to the above mentioned Rehm–Weller equation, with the half-wave redox potentials of these compounds taken into account ($E_{1/2}(\mathbf{1}) = +1.45$ V and $E_{1/2}(\mathbf{2}) = -0.66$ V (SCE)), the RIP energy levels will be 2.05 eV, while E_T of quinone **2** is 2.09 eV [18].

The sign of CIDNP effects of hydroquinone **7** (H(1,8) and H(3,6): $A = \mu(+)\times\epsilon(-)\times\Delta g(-)\times HFI(-)\times\gamma(-)$) corresponds to so-called escape product from the RIP-1 (Scheme 2). It is suggested that hydroquinone **7** is formed from the polarized radical anion of **2** ($2^{\cdot-}$) escaped from RIP. Most likely, the radical anion $2^{\cdot-}$ reacts with water (present in acetonitrile) resulting in **7** after disproportionation of two semiquinone radicals **10** (Scheme 2).

The absence of nuclear polarization effects of the initial cyclohexasilane **1**, in contrast to quinone **2**, has very important implications. This fact forces us to assume that the act of back electron transfer does not lead to the regeneration of **1**. It is reasonable to suggest that the back electron transfer occurs yet in another RIP comprised of radical anion $2^{\cdot-}$ and paramagnetic particle which is formed from **1**, but incapable to regenerate **1** in the back electron transfer step. The most reasonable candidate for this partner paramagnetic species is the open form of hexasilane radical cation ($+Si(Me)_2-Si_4(Me)_4-(Me)_2Si^+$), $11^{\cdot+}$ (RIP-2, Scheme 2). Consequently, the back electron transfer step in the RIP-2 will result in polarized quinone **2** and linear biradical **11**. As for the structure of the primary reaction product **8**, one might assume that it is formed as a result of recombination of the radical anion $2^{\cdot-}$ and radical cation $11^{\cdot+}$ in the RIP-2. The addition of **11** to oxygen atoms of quinone **2** in the bulk is also possible.

1H CIDNP analysis allows to discriminate between two possible pathways of the formation of dioxahexasilicine **8** – the recombination of RIP-2 in the singlet state or the escape product formed in the bulk on the random encounter of the partners. If the first pathway prevails, nuclear

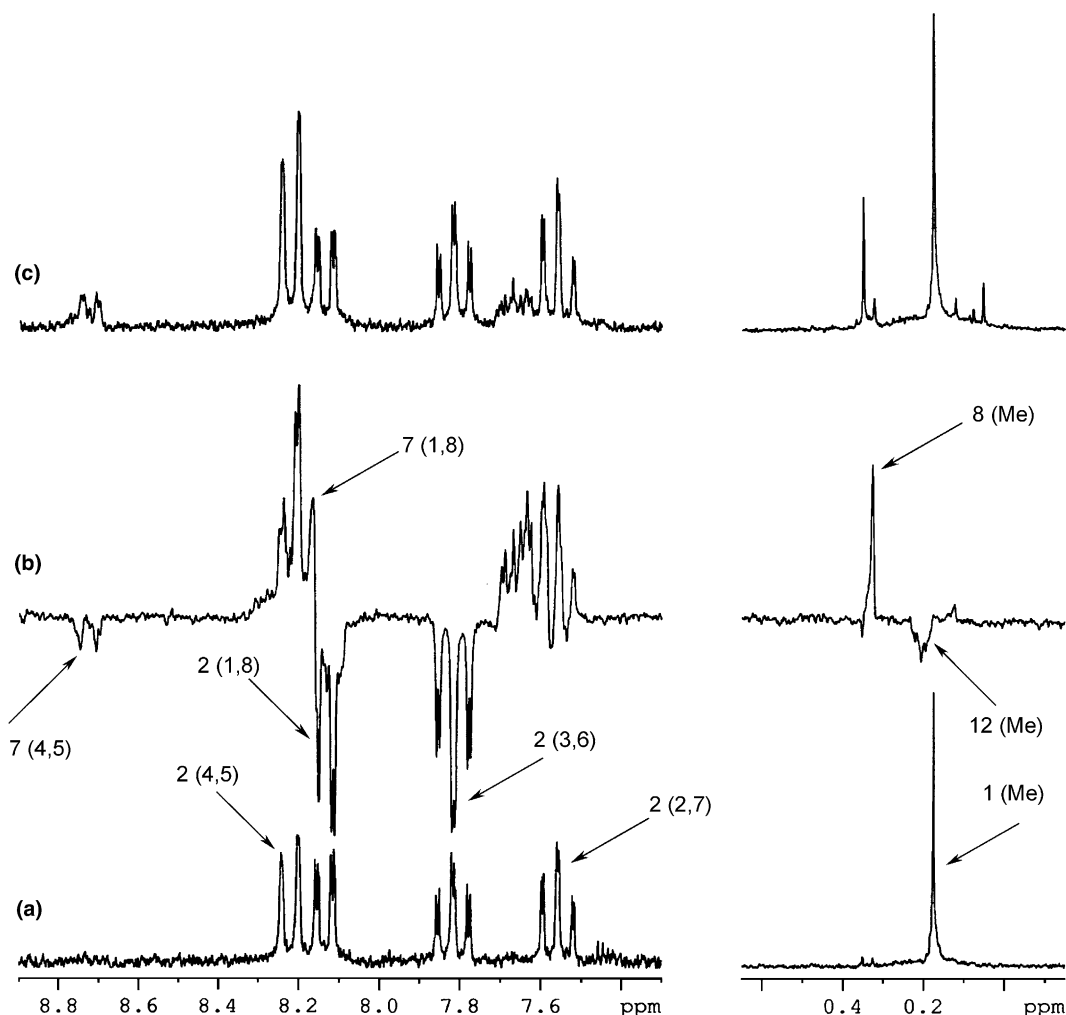
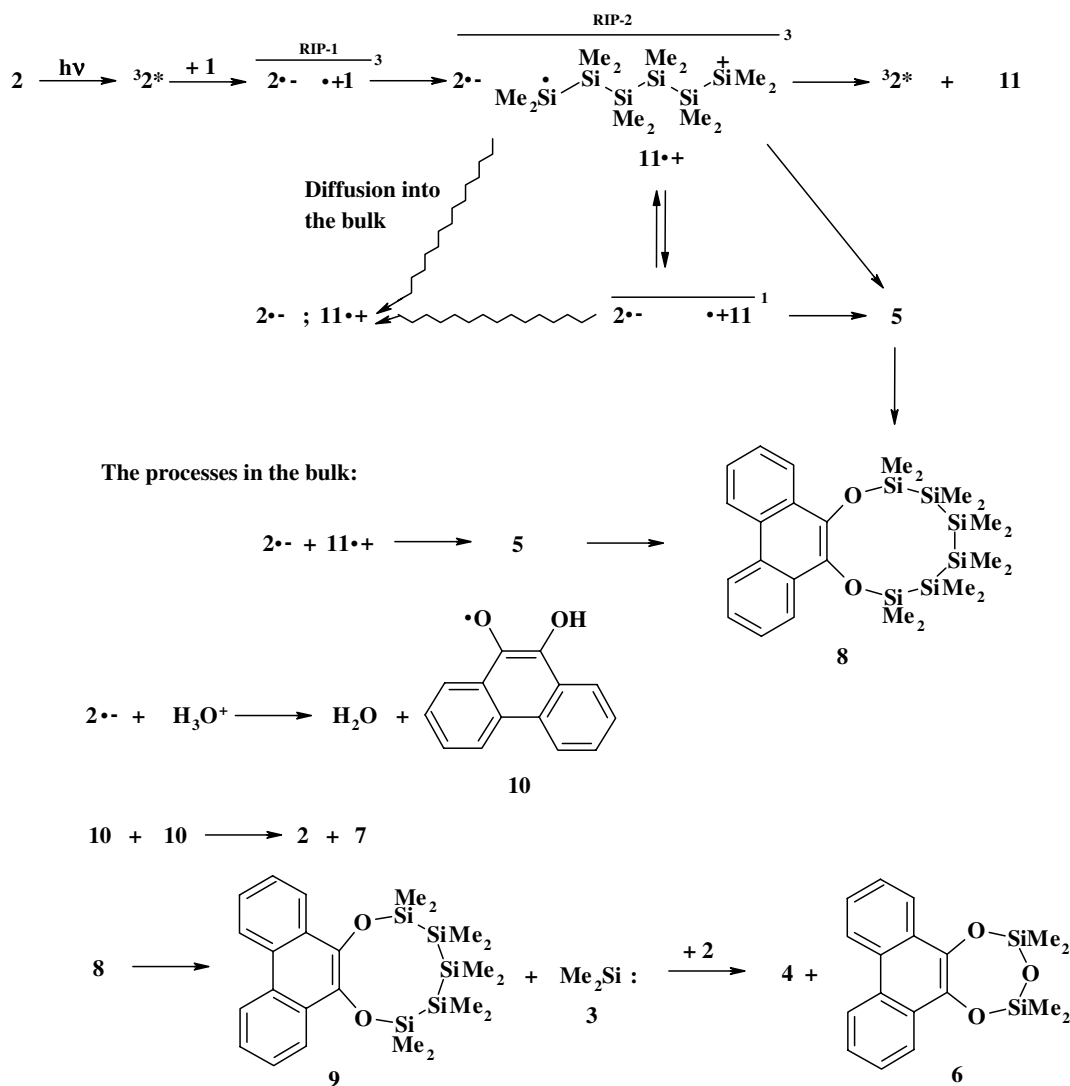


Fig. 2. 200 MHz ^1H NMR spectra of the reaction mixture of **1** and **2** in CD_3CN : (a) initial spectrum (8 sc); (b) QSS spectrum under laser irradiation (32 sc); (c) after photolysis (8 sc). The numbers in the parenthesis correspond to the proton's position in the aromatic rings.

polarization sign of methyl protons of **8** would be positive ($A = \mu(+)\times\epsilon(+)\times\Delta g(+)\times\text{HFI}(+)\times\gamma(+)$). The realization of the second pathway of the product formation in the bulk will lead to negative polarization ($E = \mu(+)\times\epsilon(-)\times\Delta g(+)\times\text{HFI}(+)\times\gamma(+)$). Unfortunately, there is also the third pathway – in the case of so-called spin-independent “charge” recombination of $\mathbf{11}^{\cdot+}$ and $\mathbf{2}^{\cdot-}$ resulting in the biradical **5**, diohexasilicene **8** might be formed from both singlet and/or triplet state of the RIP-2. One also could not exclude the appearance the chemical polarization at the stage of the transformation of unstable **8** into dioxapentasilonine **9**. Thus, additional studies needed to clarify the source of observed positive net polarization of methyl protons of **8** (Fig. 2).

To verify the above reasoning, the time-resolved (TR) CIDNP experiments have been made. TR CIDNP spectra provide the information on the sequence of the products formation, since polarization effects of the products formed in the bulk could manifest themselves with a time delay with respect to those of the products of geminate recombination.

Fig. 3 shows ^1H CIDNP spectra taken with different time delays. Here, the polarizations of the methyl protons of **8** and quinone **2** are not observed within the same time frame, and the polarized **8** appears only with 50 μs time delay. At the same time, the polarization of the protons of hydroquinone **7** is invariable with time, and its intensity remains identical for all time delays. Since hydroquinone **7** is formed only in the bulk, one might conclude that the processes in the bulk in this reaction complete within the time frame of 2 μs (duration of the single observation pulse of the NMR spectrometer). Therefore, since CIDNP effects of **8** appear with 50 μs time delay, this polarization is generated in the radical pair different from the initial one, or possibly in biradical. Indeed, it is reasonable to assume that the formation and decay stages of the unstable adduct **8** involve the intermediate step of biradical state, (e.g., **5**). Note, one might expect that the lifetime of such flexible long biradical would be long enough for the formation of the chemical polarization effects (Fig. 3). However, the experimental proofs of the above assumption are outside the scope of the present study and require separate investi-



Scheme 2. The mechanism of the photoinduced interaction between dodecamethylcyclohexasilane **1** and 9,10-phenanthraquinone **2** in polar medium according to ^1H CIDNP data.

gation. Thus, we are forced to acknowledge that the above analysis of CIDNP effects does not allow to make final discrimination between two of the three proposed mechanisms of the formation of **8** – the charge recombination in the RIP-2 or the formation in the bulk as a result of addition of $11^{\bullet+}$ to $2^{\bullet-}$, which is well-known scavenger of heavy carbenoids, silylenes and/or germylenes [22,23].

In addition to the polarized lines of quinone **2**, hydroquinone **7**, and dioxahexasilene **8**, TR CIDNP spectra show two negatively polarized signals (δ 0.183 ppm (s) and δ 2.20 ppm (s), both *E*) (Fig. 3). The latter signal (δ 2.20 ppm (s)) is attributed to water protons.

The appearance of the negatively polarized line (δ 0.183 ppm (s)) at the delay 0 μs , and insignificant changes of its intensity with the time are characteristic features of so-called “cage” product of the recombination of a radical ion or free radical pair (geminate recombination). This signal is absent in the equilibrium NMR spectra after the photolysis, so it represents certain unstable substance. Its

chemical shift is very close to that of the methyl protons of initial hexasilane **1**, this fact indicates the similarity of the structure of their alkylsilyl fragments. The observation of CIDNP of the cage product within the identical time window of the signal of polarized water allows to suggest the possibility of proton transfer from radical cation of **1** to radical anion of **2** in the RIP-1 (Scheme 3).

One might suggest that the unstable product with polarized methyl protons at δ 0.183 ppm is the silyl ether of hydroquinone (**12**). The latter could be formed via recombination of the consecutive radical pair comprised of semiquinone **10** and silene **13** radicals (Scheme 3).

The polarization of hydroxyl proton could be formed in the above mentioned radical pair of semiquinone **10** and silene **13** radicals. The most likely source of polarized water protons in the process under study are polarized hydroxyl protons of silyl ether of hydroquinone (**12**) participating in the exchange reaction with water. There is also another possibility of the explanation of the polarization of methyl

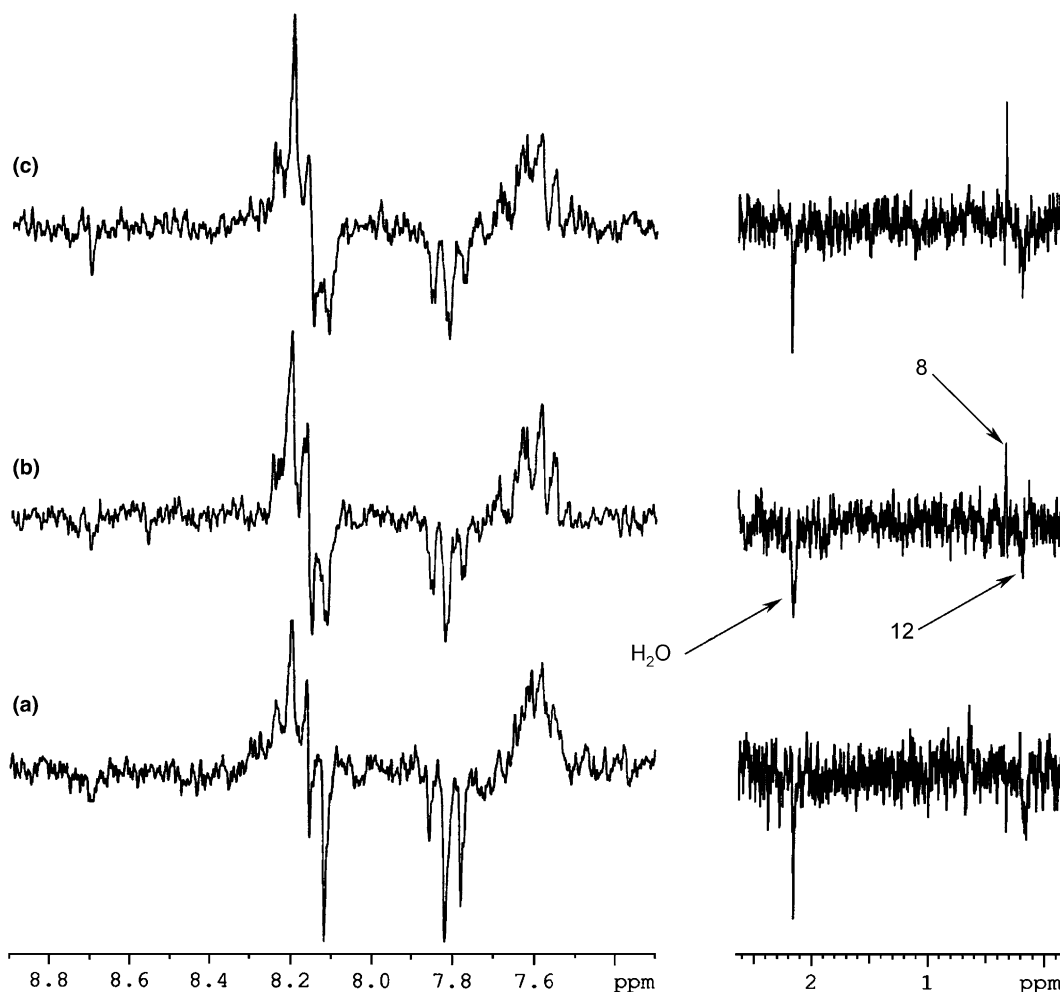
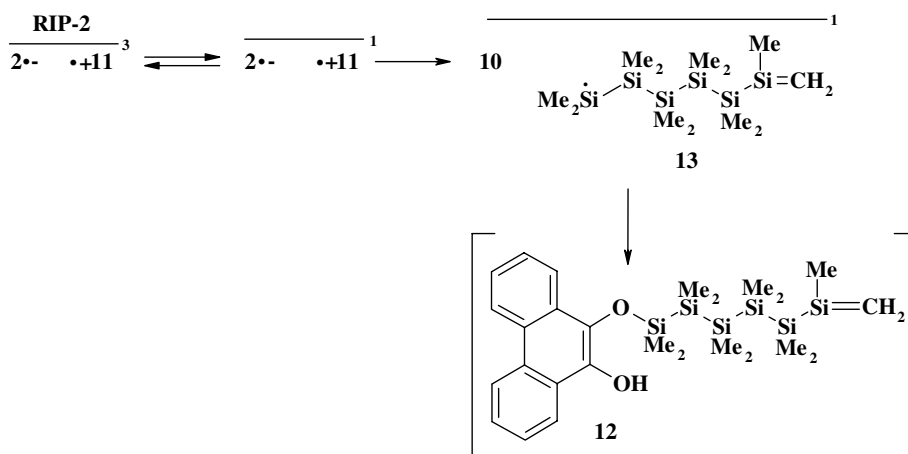


Fig. 3. 200 MHz ^1H NMR spectra of the photoreaction of **1** and **2** (1000 sc) with different time delay: (a) 0 μs ; (b) 50 μs ; (c) 500 μs .



Scheme 3. Possible mechanism of the formation of silyl ether **12**.

protons at δ 0.183 ppm, the abstraction of the polarized proton of the methyl group of $1^{\bullet+}$ by radical anion of quinone $2^{\bullet-}$. In the latter case, the polarization would be generated in the RIP-1 (see Scheme 2) and transferred to the radical pair. It is possible to make choice between these

possibilities with using CIDNP analysis. The observed negative polarizations of the methyl protons of silyl ether **12** ($E = \mu(-) \times \varepsilon(+)$ $\times \Delta g(+)$ $\times \text{HFI}(+) \times \gamma(+)$) and water protons ($E = \mu(-) \times \varepsilon(+)$ $\times \Delta g(-)$ $\times \text{HFI}(-) \times \gamma(+)$, HFI of hydroxyl protons of semiquinone radical is negative) lead

to the conclusion that their likely source is the cage product of the singlet RP which is preceded by RIP, since as it was been shown above, cage CIDNP effects formed in a singlet state of RIP - 1 should be positive (A) (Scheme 2).

4. Conclusion

Thus, CIDNP investigations of the photoinitiated reaction between **1** and **2** in the polar solvent leads to the following conclusions on the reaction mechanism.

The first stage of this process is single electron transfer resulting in the triplet RIP composed of phenanthraquinone radical anion and cyclohexasilane radical cation. This data completely agrees with the suggestion made earlier [18]. The results of CIDNP investigations point at two possible reaction pathways for the radical cation of **1**. After the back electron transfer in the RIP it transforms into silicon-centered biradical **11**. Also the radical anion of **2** is capable to abstract the proton from radical cation of **1** with the formation of semiquinone radical **10** and the silene derivative **13**. In any case, the regeneration of **1** in the RIP does not take place.

On the basis of CIDNP effects analysis, it was shown that the end reaction product dioxasilole **4** is not formed in the act of RIP recombination as it has been proposed earlier [18]. Dioxasilole **4** is the secondary product of the decomposition of dioxahexasilene **8** which is decomposed via sequential eliminations of dimethylsilylene **3**.

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