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Photolysis of 7,8-digermabicyclo[2.2.2]octadiene. The investigation of the elementary stages by means of ^{1}H CIDNP and laser pulse photolysis

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Abstract

Photolysis of 7,8-digermabicyclo[2.2.2]octadiene (**I**) was studied by means of ^{1}H-CIDNP and laser pulse photolysis techniques. It was found that photodecomposition of **I** occurs via germanium-centered 1,6-biradical species. 1,4-Diphenylnaphthalene and tetramethyldigermene are the primary products of the photolytic reaction.

Keywords: Germanium; Digermabicyclooctadiene; Dimethylgermylene; Tetramethyldigermene; Laser flash photolysis; CIDNP

1. Introduction

The investigation of the reactivity of short-lived paramagnetic intermediates in the reactions of organometallic species with Group 14 elements (in particular, silicon and germanium) is one of the topical problems in current research [1,2]. Heavy carbene analogues (silylenes, germylenes) and their dimers, the corresponding disilenes and digermenes, are the most interesting among these intermediates.

The molecules containing the Si–Si or Ge–Ge bond are known to be the potential precursors of both types of above-mentioned species [1]. It has been shown that spin chemistry methods are one of the most promising physical methods for the investigations of short-lived (from nano- to microsecond time scale) paramagnetic intermediates, and their structure and reactivity in solution [2,3]. Recently, we have shown how the combination of two spin chemistry methods, CIDNP and the magnetic field effect on the product yields, allows one to identify all major elementary stages in the photolysis of 7-silanorbornadiene derivative [3].

Here we present the results of the investigation of photodecomposition of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (**I**) by means of ^{1}H-CIDNP and laser pulse photolysis. CIDNP investigations have also been performed in the presence of the corresponding digermene and germylene scavengers.

2. Experimental

The photolysis of 7,8-digermabicyclooctadiene **I** has been carried out directly in the NMR spectrometer probe (JEOL FX 90Q, 90 MHz for ^{1}H). ^{1}H-NMR spectra were taken prior to, during, and after the photolytic reaction, using a high-pressure mercury lamp (500 W) as the UV source. The concentration of the standard solution was 2×10^{-2} M. The solvent, C_6D_6 ('Izotop') was used as supplied. 3,3,6,6-Tetramethyl-1-thiacyclohept-4-yne [4] and 7,8-digermabicyclooctadiene **I** [5] were synthesized according to the published procedures. Prior to irradiation, all samples were purged with Ar for 15 min to remove residue oxygen in

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Table 1
^{1}H-CIDNP effects observed in the photolysis of 7,8-digermabicyclooctadiene **I** in C_6D_6

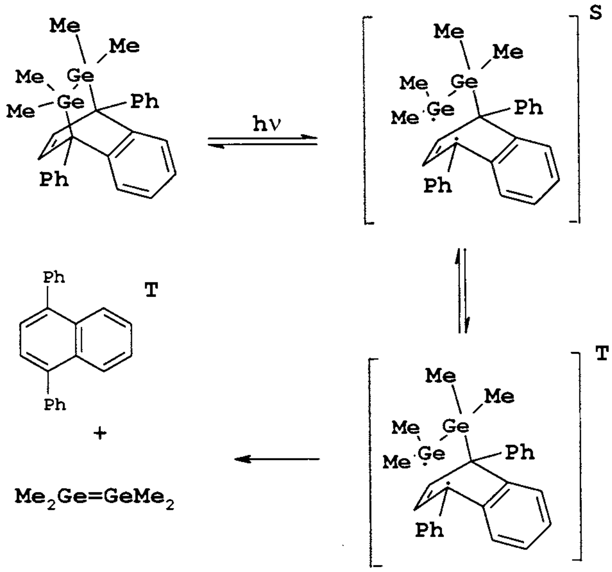
Compound	δ (ppm) (multiplicity)	CIDNP effects
I (CH_3)	0.35(s), 0.51(s)	E
I (H_5,H_6)	6.15 (s)	E
1,4-diphenylnaphthalene	7.43 (s)	A(weak)

solution. All experiments have been performed at the room temperature.

The laser pulse photolysis experiments have been performed using the submicrosecond pulse photolysis setup, with a XeCl excimer laser ($\lambda = 308$ nm, average pulse energy about 10 mJ, pulse delay 50 ns) used as the excitation light source. Detailed information on this setup can be found elsewhere [6]. All measurements were performed in a quartz optical cell, $l = 1$ cm. Typical concentration of the solution of 7,8-digermabicyclooctadiene **I** in hexane was 2.5×10^{-3} M.

3. Results and discussion

The photolysis of 7,8-digermabicyclooctadiene **I** in solution was investigated by means of the ^{1}H-CIDNP method and allowed observation of the polarization of H(5), H(6), and $-CH_3$ group protons of **I** and phenyl protons of 1,4-diphenylnaphthalene (see Table 1). According to ^{1}H-NMR data, the end products of the reaction are 1,4-diphenylnaphthalene and germanium-containing oligomers (Fig. 1).



Scheme 1.

It should be pointed out that the CIDNP effects in the system under study are identical to those observed under similar conditions during the photodecomposition of monogermanium analogue, the 7,7-dimethyl-1,4,5,6-tetraphynyl-[2,3]-benzo-7-germanorbornadiene [2]. Indeed, similar nuclear polarization effects were detected in Ref. [2]: the emission of methyl protons of the initial 7-germanorbornadiene, and the absorption of aromatic protons of 1,2,3,4-tetraphenylnaphthalene. As it has been shown earlier [2,3], the manifestation of chemical polarization of the initial compound is evidence of CIDNP formation in 1,5-biradicals generated

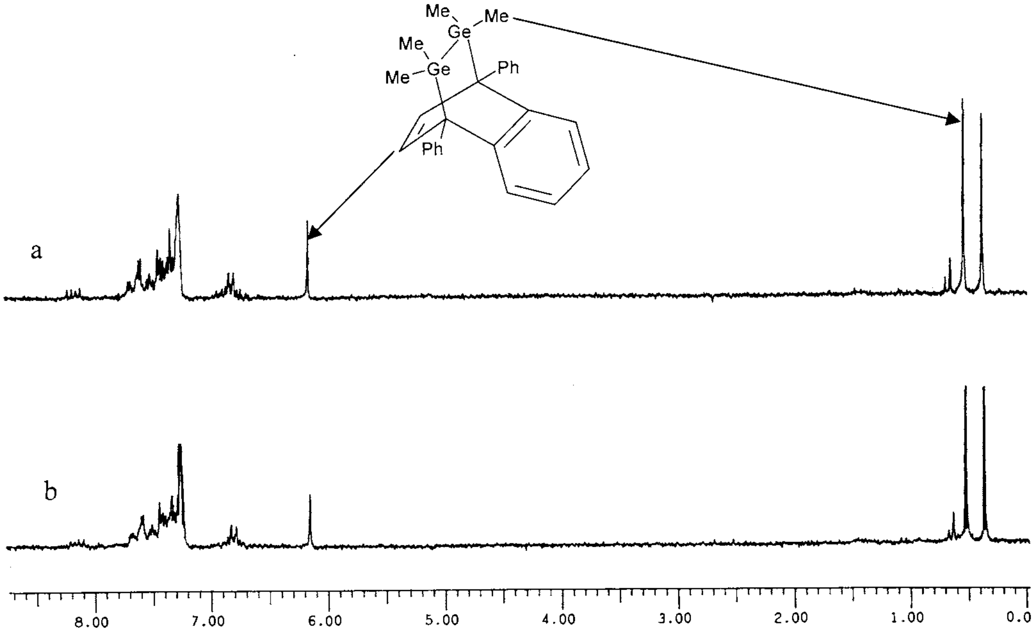


Fig. 1. ^{1}H-CIDNP effects observed in the photolysis of 7,8-digermabicyclooctadiene **I** in C_6D_6: (a) initial spectrum; (b) spectrum under UV irradiation (20 s).

through the photochemical cleavage of element-carbon bond in 7-heteronorbornadienes. The opposite signs of the polarization effects in the initial compound and in the product points to the formation of CIDNP effects via $S-T_0$ mechanism. The application of Kaptein rules [7] for analysis of CIDNP effects in the photolysis of **I** shows that the initial 7,8-digermabicyclooctadiene **I** is regenerated via the recombination of the singlet 1,6-biradical, while its triplet state further decays to 1,4-diphenylnaphthalene in triplet excited state and tetramethyldigermene. The generation of triplet excited product from triplet biradical is dictated by the full spin retention rule (Scheme 1).

Verification of the suggested scheme has been carried out by means of laser pulse photolysis of solutions of **I** in C_6D_6. The first laser excitation pulse produced a very intense absorption signal. Its characteristic maximum at 420 nm agrees with the reference data on T–T absorption of 1,4-diphenylnaphthalene [8] (Fig. 2).

However, we have not managed to detect any signals around 370 nm, which should be characteristic for digermene [9]. This could possibly be explained by a significant difference in molar extinction coefficients of these two products. The detection of triplet excited state of 1,4-diphenylnapthalene is an additional confirmation of the suggested Scheme 1.

Unfortunately, these experimental findings do not allow an unambiguous conclusion to be drawn on the proposed mechanism of the decomposition of **I** (Scheme 1). One also should not exclude the alternative (or parallel) reaction involving sequential generation of two molecules of dimethylgermylene (Scheme 2).

In this case, the initial 1,6-biradical decomposes through Ge–Ge bond cleavage rather than Ge–C one leading to Me_2Ge generation. The resulting 1,5-biradical, a well-known intermediate of the photolysis of 7-germanorbornadiene derivative [2], either recombines to 7-germanorbornadiene (**II**) or decomposes to 1,4-diphenylnaphthalene and Me_2Ge after Ge–C bond

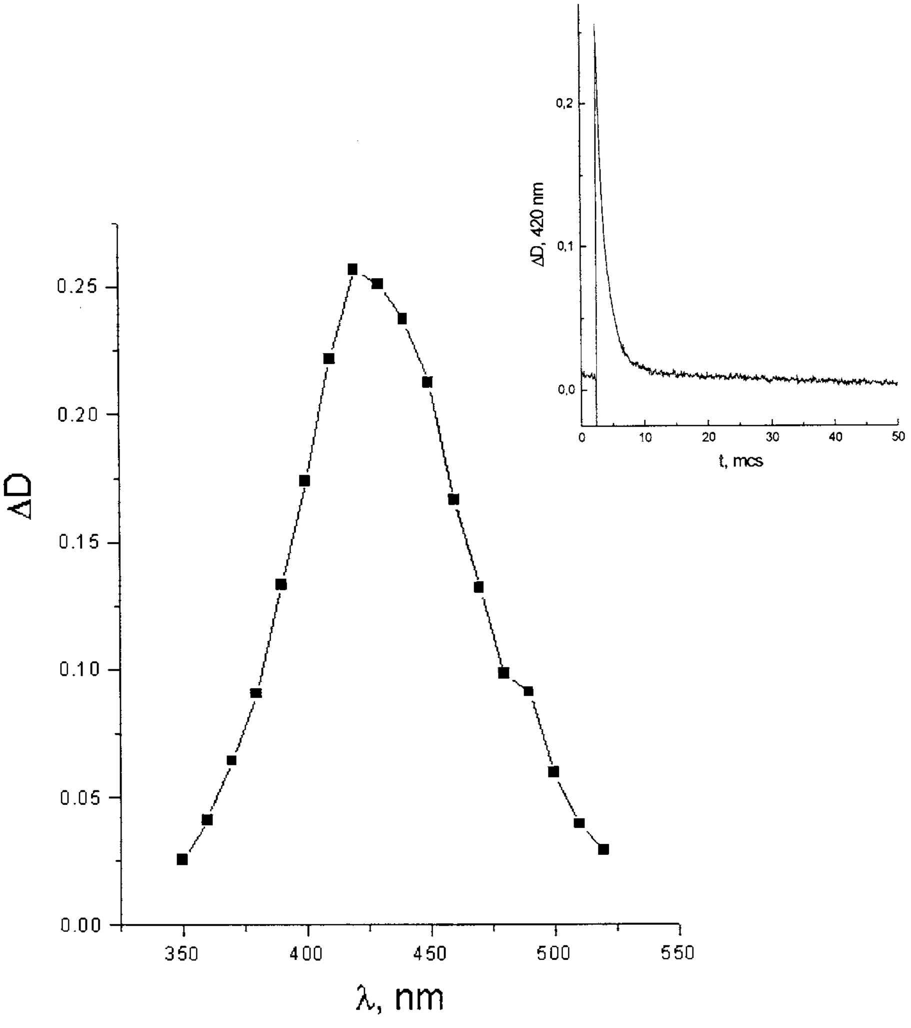
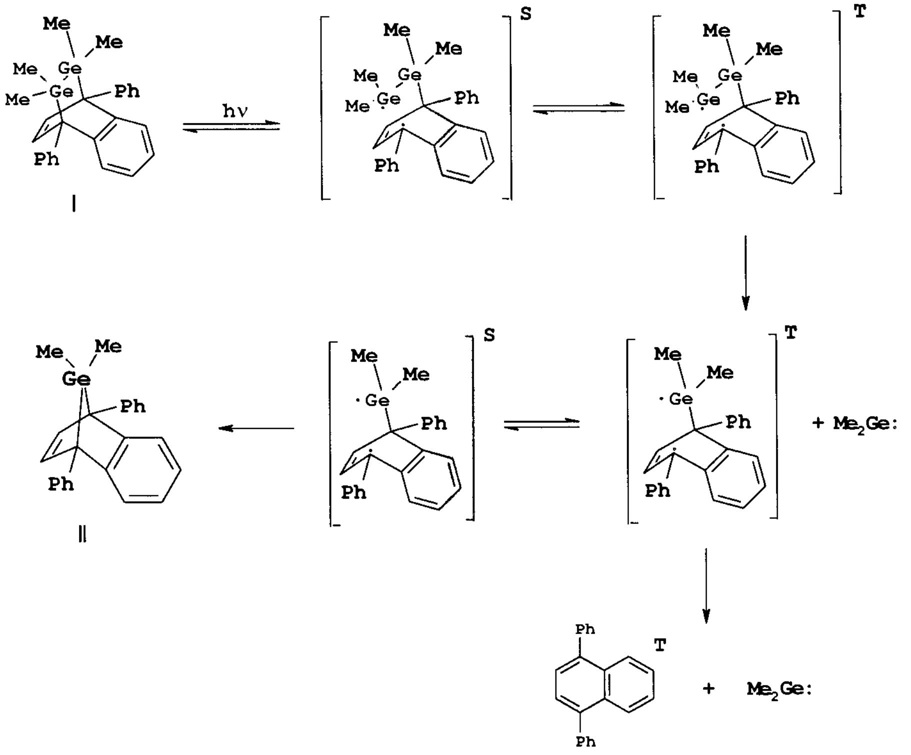


Fig. 2. Laser pulse photolysis of **I** in hexane. Triplet absorption spectrum of 1,4-diphenylnaphthalene (average of four laser pulses). Inset: kinetic trace taken during the photolysis of **I** at $\lambda = 420$ nm.



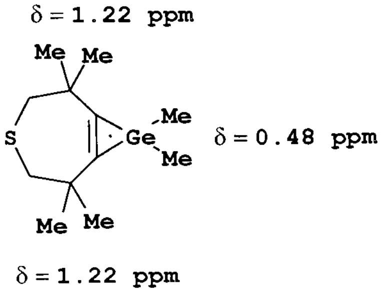
Scheme 2.

cleavage. In the framework of the suggested mechanism tetramethyldigermene is formed through the dimerization of Me_2Ge.

If the pathway shown in Scheme 2 is realized, one might expect to observe the characteristic signals of Me-protons of 7-germanorbornadiene **II** in the NMR spectra. However, under our experimental conditions these lines are absent, probably because of the high photochemical lability of 7-germanorbornadiene (Fig. 1). Note that the lack of 7-germanorbornadiene **II** signals in the NMR spectra does not necessarily imply the absence of Me_2Ge in the reaction under study, since according to [1] the interconversion between Me_2Ge and $Me_2Ge{=}GeMe_2$ could occur in solution.

To identify the short-lived germanium-containing intermediates of the photolysis of **I**, the investigation of ^{1}H-CIDNP effects in the presence of germylene and digermene scavenger has been carried out. In addition to the CIDNP effects discussed above (Table 1), three polarized signals are observed in CIDNP spectra during the photolysis of **I** in the presence of one of the most effective Me_2Ge scavengers, 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne [2b] (Fig. 3).

Two signals are located downfield (positively polarized singlet, 1.22 ppm) and upfield (1.13 ppm) from the methyl group of thiacycloheptyne (1.15 ppm), and the third (positively polarized singlet, 0.48 ppm) is close to the signals of methyl protons of **I**. The signals at 1.22 and 0.48 ppm are identical to the signals of the product of dimethylgermylene addition to the triple bond of thiacycloheptyne detected earlier during the photolysis of 7-germanorbornadiene derivative [2]. The cycloadduct (germirene) has the following structure:



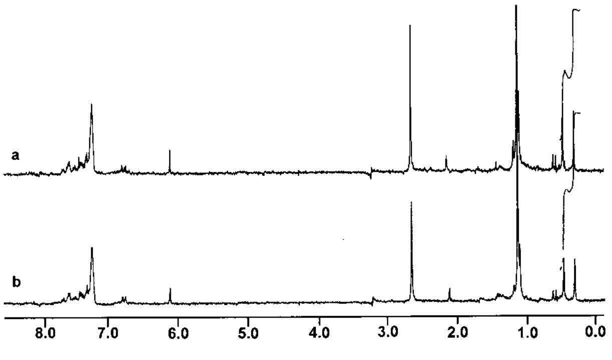


Fig. 3. ^{1}H-CIDNP effects detected during the photolysis of 7,8-digermabicyclooctadiene **I** in the presence of thiacycloheptyne in C_6D_6: (a) spectrum under UV irradiation (30 s); (b) dark spectrum after irradiation. Integrals are shown to illustrate polarization of the initial **I**.

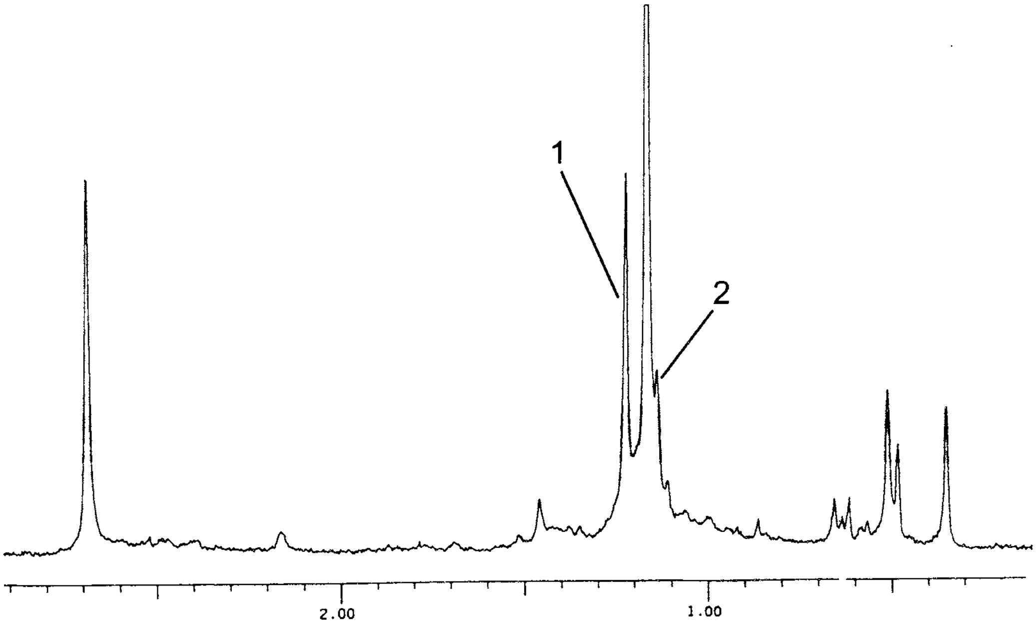
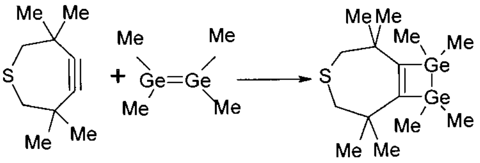


Fig. 4. Products after prolonged photolysis (5 min) of the reaction mixture shown in Fig. 3 (1) — methyl groups of germacyclopropene **II**, (2) — methyl groups of 1,2-digermacyclobutene **III**. Cf. the ratio of the intensities of these species in Fig. 3.



III

Scheme 3.

It has been suggested earlier [2] that CIDNP effects arising from the protons of this adduct are formed in the intermediate 1,3-biradical generated by the addition of dimethylgermylene to triple bond of thiacycloheptyne. According to Kaptein rules [7], the positive polarization we observed testifies to the reaction of thiacycloheptyne with the triplet excited dimethylgermylene, Me_2Ge^T. Similar behavior has been reported for dimethylgermylene generated by the photolysis of 7,7-dimethyl-1,4,5,6-tetraphynyl-2,3-benzo-7-germanorbornadiene [2].

One might also suggest reasonably that the additional signals (at 1.13 and 0.88 ppm) detected in the reaction under study are attributed to the cycloadduct of tetramethyldigermene and thiacycloheptyne (Scheme 3), the 1,2-digermacyclobutene (**III**). The signals are very close to those of 1,2-digermacyclobutene **III** reported previously [10]. Judging from NMR spectra, at the initial stages of the photolysis of **I** in the presence of thiacycloheptyne, this adduct seems to be the major reaction product. However, after 5 min of continuous UV irradiation the germacyclopropene becomes the prevailing product (Fig. 4). This points to a relatively low photochemical stability of the 1,2-digermacyclobutene **III**. In addition, after the prolonged photolysis, NMR spectra of the reaction mixture demonstrated the accumulation of germanuim-containing oligomers (δ 0.5–0.7 ppm, Fig. 4).

Thus, NMR and ^{1}H-CIDNP investigations of the photolysis of **I** in the presence of thiacycloheptyne demonstrate the involvement of two germanium-containing intermediates, dimethylgermylene and tetramethyldigermene. One might suggest that the source of dimethylgermylene in the system under study is tetramethyldigermene. The basis for this assumption is the well-known instability of digermenes [1], and the CIDNP effects observed for 1,2-digermacyclobutene **III** and germacyclopropene moieties. Moreover, the radical mechanism drawn on the basis of all experimental data (Scheme 1) also speaks in favor of the assumption that digermene is a primary product of photochemical decomposition of **I**.

4. Conclusions

The similarity of CIDNP effects observed during the photolysis of 7-germanorbornadiene derivative and 7,8-digermabicyclooctadiene **I** as well as T–T absorption of the main reaction product, 1,4-diphenylnaphthalene, show that photodecomposition of **I** occurs via a germanium-centered 1,6-biradical. 1,4-Diphenylnaphthalene and tetramethyldigermene are primary products of the photolytic reaction. The ultimate conclusion about the source of dimethylgermylene in this reaction might be drawn only after investigations of the photolysis of **I** in the presence of the other scavengers of heavy carbene analogues.

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