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Spin chemistry of short-lived intermediates in the reactions of germanorbornadiene derivatives and digermabicyclooctadiene

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The review concerns the potentialities of chemically induced dynamic nuclear polarization technique (a spin chemistry method) in studies of elementary processes with participation of short-lived organogermanium species, *viz.*, dimethylgermylene and tetramethyldigermene. The photogeneration and trapping mechanisms of the species in the presence and in the absence of various trapping agents in solutions are considered.

Key words: dimethylgermylene, tetramethyldigermene, biradicals, photochemistry, spin chemistry.

1. Introduction

Research on reactive short-lived paramagnetic and diamagnetic germanium-containing species, such as germylene derivatives and compounds with the multiple Ge=X (X = Ge, N, P, O) bonds, has attracted considerable attention in the last two decades. One of the main problems of physical organic chemistry is to establish the elementary mechanisms of processes that are thought to proceed with participation of these intermediates.[1—4] Often, to solve this problem is simply to decide between the radical and ionic mechanisms taking into account arguments in favor of each of them. It is undoubtful that the most reliable method of attacking the problem is to identify the short-lived intermediates that are precursors of the end reaction products.

Analysis of the available information obtained in studies of intermediates of the reactions of various organometallic compounds reveals that this can be done using two different main approaches. The first approach, typical of classical organic chemistry, implies drawing conclusions about the structure of intermediate short-lived species and their possible involvement in a reaction under study on the basis of detailed analysis of the composition of end products. The second, physicochemical, approach is based on the results of kinetic studies that are used for measuring the rate constants for reactions with participation of intermediates. In many instances, such studies are carried out without analyzing the chemical composition of the products of the reaction under study. Unfortunately, it should be noted that often spectrophotometric and kinetic information on the intermediates of the reactions proceeding with participation of short-lived derivatives of Group 14 elements is contradictory and depends on both the experimental conditions and the properties of the precursor molecules. This can be shown taking the spectral characteristics of the simplest short-lived alkyl-substituted carbenoid, dimethylgermylene, reported by different authors (Table 1) as an example.

Table 1. Spectroscopic characteristics of dimethylgermylene

Precursor	Reaction conditions		λ_{max} /nm	Reference
	T/K	Solvent		
$Me_2Ge(SePh)_2$	21	Ar	420	5
	77	3-MP*	420	5
	293	*cyclo*-C_6H_{12}	420	5
	293	CCl_4	420	5
$(Me_2Ge)_5$	77	3-MP	506	6
	293	*cyclo*-C_6H_{12}	490	6
$(Me_2Ge)_6$	77	3-MP	430	7
	293	*cyclo*-C_6H_{12}	450	7
$PhGeMe_2SiMe_3$	293	*cyclo*-C_6H_{12}	425	8
1	293	C_7H_{16}	380	2
$Me_3GeGeHMe_2$	293	Gas phase	480	9

* 3-MP stands for 3-methylpentane.

Meanwhile, there is yet another group of physical methods that use the dependences of the rates of the processes involving paramagnetic species on the electron-nuclear interactions in these intermediate species. These are the spin chemistry methods, *viz.*, the chemically induced dynamic nuclear polarization (CIDNP) and the magnetic effect (ME).[10] Sometimes, they can provide reliable information on the nature of the paramagnetic intermediates formed in the reactions under study and their further transformations. The main advantage of the CIDNP technique consists in the combination of the simplicity and reliability typical of structural analysis of the reaction products using NMR spectroscopy methods and high sensitivity of chemical polarization.

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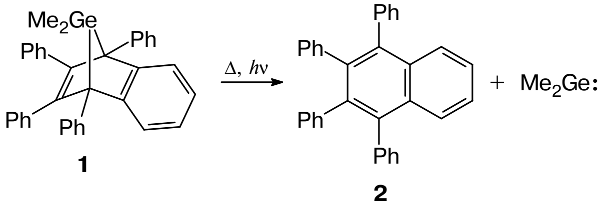
We believe that currently it is joint use of the spin chemistry methods and laser pulse photolysis that can provide the most valuable information on the formation and trapping reactions of such reactive short-lived derivatives as alkyl-substituted germylenes and digermenes and germanium-centered free radicals.[2,11–13]

In this review we consider the results of application of these methods to the investigation of the chemical reactions involving dimethylgermylene and tetramethyldigermene generated in the photodecomposition of germanium-containing bicyclic compounds, 7-germanorbornadiene and 7,8-digermabicyclooctadiene.

2. Generation of dimethylgermylene

7-Germanorbornadiene derivatives belong to the most appropriate and widely used precursors of germylene.[1,2,11–16] Under mild thermal conditions or upon UV irradiation they decompose into an inert aromatic molecule and a short-lived carbenoid. This is illustrated in Scheme 1 taking the generation of dimethylgermylene from 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germanorbornadiene (**1**) as an example.

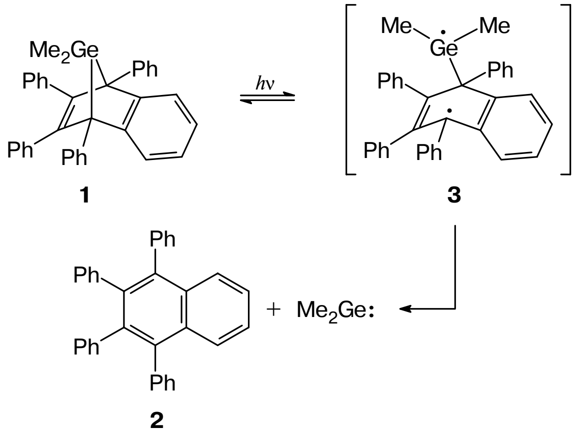
Scheme 1



The hypothesis that this reaction can proceed with participation of biradicals that are formed by the cleavage of one of the Ge—C bonds has been discussed for long.[1] Studies of the thermal decomposition of compound **1** monitored by NMR spectroscopy[11] or using the absorption spectrum of 1,4,5,6-tetraphenylnaphthalene (TPN, **2**)[14] revealed that the reaction proceeds as a first-order process with the rate constant $k = 1.1 \cdot 10^{-3}$ s^{-1} (78 °C, toluene).[14] The order of magnitude for the activation parameters of this reaction ($\Delta H^{\neq}$ = 27.8 kcal mol^{-1}, $\Delta S^{\neq}$ = 6.8 cal mol^{-1} K^{-1} in the temperature range between 65 and 85 °C) is in agreement with the known data on the reactions proceeding by biradical mechanism.[14] Unfortunately, an attempt at detecting a germanium-centered biradical using ESR spectroscopy failed, which can be due to both short lifetime and low concentration of the biradical.[1]

Generation of germylene in the photodecomposition of germanorbornadiene **1** was also studied by flash photolysis and matrix isolation methods.[2,13] The appearance of an absorption band with a maximum at λ = 420 nm in the low-temperature photolysis of **1** (77 K) was associated with the formation of 1,5-germanium-centered biradical.[13] This conclusion was based, first of all, on the fact that species responsible for the absorption spectrum with a maximum at λ = 420 nm was transformed into the initial norbornadiene **1** upon annealing. The following scheme of dimethylgermylene generation was proposed (Scheme 2).[13]

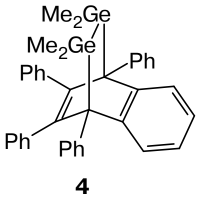
Scheme 2



Confirmation of the hypothesis for the formation of biradical and further detalization of the scheme of the photolysis of **1** had become possible after performing ^{1}H CIDNP studies.

According to ^{1}H NMR and GLC studies, photolysis of **1** in solutions of C_6D_6, C_6D_{12}, $CDCl_3$, and CD_2Cl_2 and in a CCl_4—C_6D_6 mixture results in compound **2** and oligogermanes (they are formed as a result of further transformations of dimethylgermylene) as the end products. In the presence of halogen-containing solvents, reaction products of Me_2Ge with solvent molecules are also detected (see below).

The rate constant for the reaction between dimethylgermylene and initial norbornadiene **1** is known[17] to be relatively high ($k = 1.2 \cdot 10^7$ L mol^{-1} s^{-1}).[13] However, the addition product of Me_2Ge to **1**, 1,4,5,6-tetraphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (**4**), can be detected using NMR spectroscopy only if the initial **1** is photolyzed in the presence of CCl_4. In the case of photolysis of structurally similar 7-silanorbornadiene for which the insertion reaction of dimethylsilylene ($k = 5.7 \cdot 10^9$ L mol^{-1} s^{-1}) was also reported,[18] disilabicyclooctadiene not only can be detected by NMR spectroscopy but also exhibits CIDNP effects.[19]



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The CIDNP effects recorded during the photolysis of **1** in deuterobenzene are shown in Fig. 1 and collected in Table 2. Analogous CIDNP effects were observed in the photolysis of **1** in all the above-mentioned solvents and in the photolysis of 7-silanorbornadiene.[12]

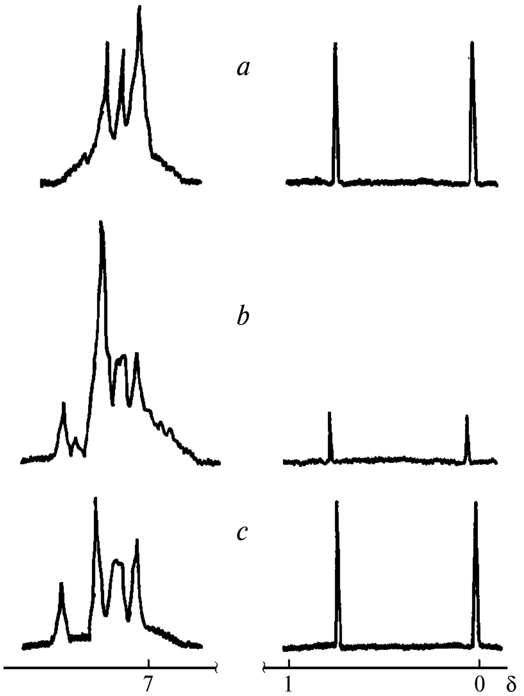


Fig. 1. ^{1}H CIDNP effects in the photolysis of 7-germanorbornadiene **1** in C_6D_6: initial spectrum (*a*); spectrum recorded during irradiation (*b*); and spectrum after irradiation (*c*) (see also Table 2).

Table 2. ^{1}H CIDNP effects in the photolysis of **1** in C_6D_6

Compound	δ	Assignment	CIDNP effects*
1	0.22, 0.94 (both s)	$GeMe_2$	E
2	7.43 (s)		A

* Here and in Tables 3 and 5—8 E stands for emission and A stands for absorption.

Manifestation of CIDNP effects of protons of the initial compound points to the reversibility of the photodecomposition of compound **1**, which confirms the hypothesis for the formation of 1,5-biradical.[13]

Analysis of polarization effects was performed using the rules derived in the framework of the theory of radical pairs (RP)[10] for the description of CIDNP effects and known as Kaptein's rules.[20] For the net polarization in strong magnetic fields the sign of the CIDNP effect (Γ) depends on the parameters of radicals involved in the reaction and is determined by the sign (sgn) of the product of the following factors:

$$\Gamma = \mathrm{sgn}(\mu \cdot \varepsilon \cdot A_k \cdot \Delta g), \qquad (1)$$

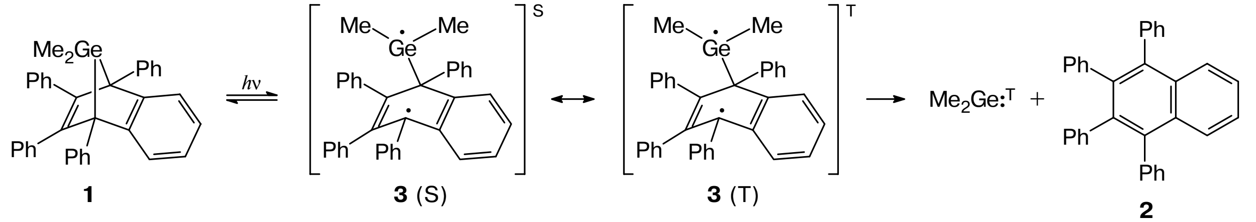
where Δg is the g-factor difference between the partner radicals of the RP; A_k is the constant of isotropic HFC with the nucleus under study; ε is the factor characterizing the formation mechanism of the compound under study ($\varepsilon > 0$ if the product is formed in recombination of the RP and $\varepsilon < 0$ if the product is formed in the reaction of radicals that escaped from the RP to the bulk); and μ is the factor characterizing the multiplicity of the RP to be formed ($\mu > 0$ for the triplet pair and $\mu < 0$ for the singlet pair). The signs of the CIDNP effect, "+" and "−," mean positive (absorption, or spectrum of the type A) and negative polarization (emission, or spectrum of the type E), respectively.

The CIDNP effects in question were analyzed assuming that the magnetic resonance parameters of the biradical **3** formed in the photoreaction are as follows: (i) the g-factor of the germanium-centered fragment of 1,5-biradical **3** is comparable in magnitude with the g-factor of trimethylgermyl radical ($g(Me_3Ge^{\bullet}) = 2.0104$) and (ii) the g-factor of the second fragment of the 1,5-biradical is close to 2.0025, which is typical of hydrocarbon radicals.[21]

Analysis of the CIDNP effects observed in the photolysis of compound **1** showed that the 1,5-germanium-centered biradical **3** is formed in the singlet state. Recombination of **3** provides the possibility for the initial molecule to regenerate, and an emission signal is observed of methyl protons of norbornadiene **1**: $\Gamma = -$ ($\mu < 0$, $\varepsilon > 0$, $a > 0$, $\Delta g > 0$). In this case, the observation of absorption of protons of the main stable reaction product **2** means that it was formed from the triplet state of the 1,5-biradical: $\Gamma = +$ ($\mu > 0$, $\varepsilon < 0$, $a > 0$, $\Delta g < 0$). According to the total spin conservation rule in the system, one of the decomposition products of triplet biradical **3** should be formed in the triplet state. It was reasonable to assume that such a product is dimethylgermylene, which is formed after cleavage of the second Ge—C bond in biradical **3** simultaneously with the formation of **2**. The results of laser pulse photolysis studies of the structurally similar 7-silanorbornadiene showed that compound **2** is formed in the singlet ground state.[18] We will emphasize that no generation of triplet carbenoids was reported until the experiments[12] on the observation of CIDNP effects in the photolysis of 7-heteronorbornadienes were carried out. In the study of the photolysis of 7-silanorbornadiene definite conclusions about the formation of dimethylsilylene in the triplet state were drawn on the basis of not only qualitative analysis of CIDNP effects, but also quantitative measurements of the magnetic effects detected in this system by pulse laser photolysis.[19] The complex character of this study substantially improves the reliability of the conclusions drawn. Since the experiments on the photolysis of 7-heteronorbornadienes have led to the observation of analogous CIDNP effects, one can infer that the results obtained for the silicon-containing analog improve the reliability of the mechanism presented in Scheme 3.

Meanwhile, no CIDNP effects of the initial compound were observed in the thermal decomposition studies of germanorbornadiene **1**.[11,22] The effects detected were those formed in the RP by a germyl free radical that was generated *via* abstraction of an atom of the

Scheme 3



scavenger molecule by singlet germylene. This distinction can be explained both by the lower concentration of the thermally generated paramagnetic species (compared to photolytically generated ones) and by specific features of the procedure chosen for the observation of CIDNP effects[11,22] (it needs longer time intervals that precede the recording of CIDNP effects in such experiments). The possibility for changing the reaction mechanism during the thermolysis of **1** (*e.g.*, a simultaneous cleavage of two Ge—C bonds by a concerted mechanism) cannot also be ruled out. In this case, CIDNP effects will be observed only for the reaction products of dimethylgermylene with trapping agents.

In addition to the situation described by Scheme 3, CIDNP effects of the initial compound **1** can also be observed if we assume that norbornadiene **1** can be formed in the reaction of dimethylgermylene with the end product, TPN (**2**). However, this reaction proceeds in the bulk, and, hence, the presence of additional amount of germylene scavengers must affect the CIDNP efficiency. However, CIDNP effects of the initial compound **1** are known to be independent of germylene scavengers (see Section 3). No such reaction of dimethylgermylene with naphthalene derivatives was also detected in the thermal decomposition study of **1**.[1,17]

Let us consider the applicability of Kaptein's rules (1) to strong fields (the S—T_0 approximation), since generally these rules were not derived for the description of CIDNP effects formed in biradicals. According to the RP theory, the observation of CIDNP effects with opposite signs for the methyl and phenyl protons (see Table 2) and the possibility for different products to be formed from singlet and triplet states of the biradical allows one to use Kaptein's rules.[10] The formation of CIDNP effects by the S—T_0 mechanism is possible for the so-called "rigid" biradicals.[10] In this case, we can deal with a fixed orientation of the orbital of an unpaired electron of the Ge atom with respect to the carbon skeleton of 1,5-biradical **3**. Calculations of the geometry of a structurally similar silicon-containing 1,5-biradical have been reported recently.[23] Since no other data on the structure and lifetimes of element-containing biradicals are available at the moment, the results of the CIDNP and ME experiments are of particular interest. For instance, the lifetime of biradical **3** can be estimated from the mere fact of the observation of CIDNP effects. According to the RP theory,[10] the formation of nonequilibrium population (CIDNP) in the radicals, for which the HFC constants are no greater than 5 Gs (*e.g.*, in $Me_3Ge^{\bullet}$ and $Me_3Si^{\bullet}$),[21] requires that the lifetimes of such intermediates be no shorter than several nanoseconds.

"Heavy" carbene analogs containing atoms of Group 14 elements are known to have a singlet ground state.[24] Therefore, the next step is to discuss deeper stages of the process in question, which follow the reactions shown in Scheme 3, namely, the singlet—triplet intersystem crossing of dimethylgermylene and the reaction with scavengers of Me_2Ge from both triplet and singlet states. Reactions of singlet dimethylgermylene have been much studied by different methods, whereas information on the reaction of triplet Me_2Ge is based only on the results of CIDNP experiments. In the text below we will describe the reactions of different spin states of dimethylgermylene.

3. Bulk reactions of dimethylgermylene in the presence of various trapping agents

Alkyl-substituted germylenes are known to undergo insertion into the C—X bonds (X = OH, Hal; and E is an element).[1,2] The rate constants for many reactions of carbenoids, determined by laser pulse photolysis, will be used in discussing the CIDNP effects in the corresponding Sections of the review. However, this concerns the reactions of carbenoids in the singlet ground state. No reactions of triplet "heavy" carbene analogs were reported until the CIDNP experiments were carried out.

Two alternative mechanisms of insertion reactions in nonpolar solvents are a three-center concerted and a free-radical, abstraction—recombination mechanism.[1] They can be hardly distinguished based only on the analysis of the end reaction products, whereas the use of CIDNP technique often allows one to establish the reaction mechanism and to determine the multiplicity of the reacting state of the carbenoid.

Reactions of both thermally[11,22] and photochemically[12,25] generated dimethylgermylene have been studied by the CIDNP method. The presence of various trapping agents including alkyl halides was found to have little effect on the rate of the thermolysis of **1** [11,14] and on the CIDNP effects[12] of protons of the initial compound in the photolysis of **1** (see above). Hence, these scavengers do not react with the 1,5-element-centered biradical **3**.

Insertion reactions of carbenoids into the C—Hal bonds of alkyl halides appeared to be the most appropriate for CIDNP studies. It is halogen-containing scavengers that were used to obtain the main body of information on the bulk reactions of the thermally and photochemically generated dimethylgermylene. Since, according to Scheme 3, photolysis of **1** results in the formation of triplet Me_2Ge, it seems logical to begin the discussion of bulk reactions with the description of the first example of the reaction of triplet germylene.[25]

3.1. Reaction with thiocycloheptyne

Dimethylgermylene is known to undergo insertion into the triple bond of 3,3,6,6-tetramethylthiocyclohept-4-yne (**5**) to give germacyclopropene **6**.[26] The rate constant for this reaction is $k = 5 \cdot 10^8$ L mol^{-1} s^{-1}.[13] Studies of the photodecomposition of **1** in the presence of **5** by ^{1}H CIDNP revealed[25] polarized signals, *viz.*, emission for methyl groups of the initial compounds **1** and **5** and absorption for protons of the reaction product (Fig. 2, Table 3).

Based on comparison with the known data,[26] the signals with positive polarization can be assigned to molecule **6**. For this compound, the signal at δ_H 1.22 was assigned to methyl protons of the thiocycloheptyne fragment while the signal at δ_H 0.48 was assigned to the dimethylgermyl moiety. The observation of CIDNP effects of adduct **6** shows that it was formed from paramagnetic precursors. However, the formation of an RP seems to be unfeasible in this case, since this would imply abstraction of any fragment of **5** by germylene. It only remains for us to assume that the intermediate stage of germylene insertion into the triple bond of **5** involves the formation of 1,3-biradical **7**. It should be noted that it is just the mechanism of dimethylsilylene insertion into the Si—C bond of 7-silanorbornadiene. The formation of 1,6-disilabicyclooctadiene biradical in this reaction has been proved[19,28] by analyzing the dependence of the yield of the photolysis product (TPN, **2**) on the external magnetic field strength.

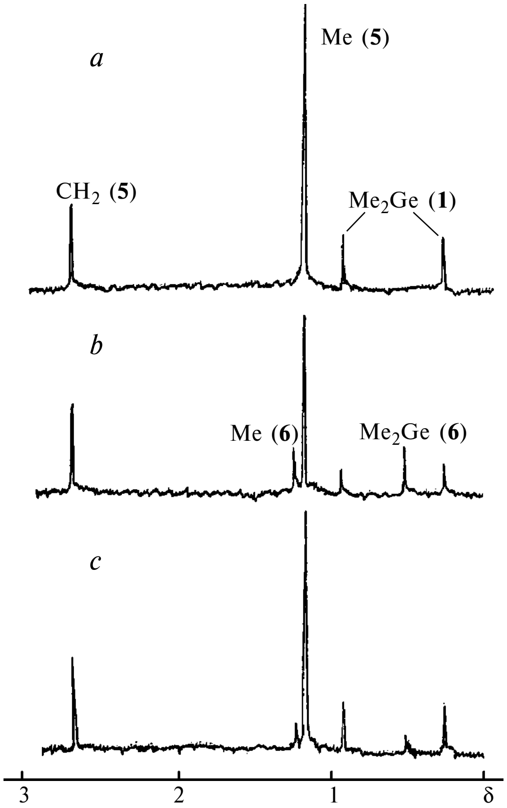


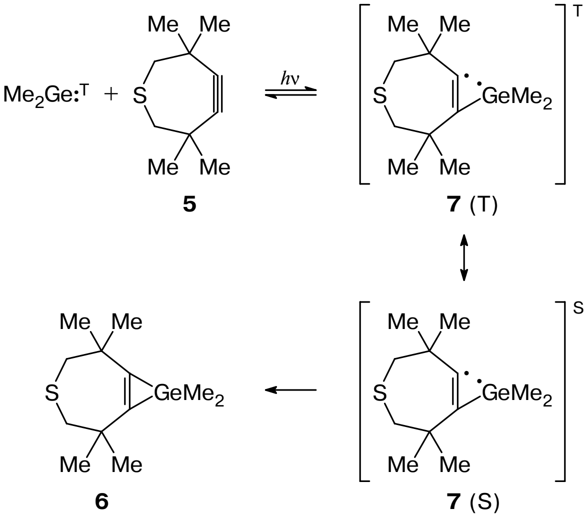
Fig. 2. ^{1}H CIDNP effects in the photolysis of **1** in the presence of **5** in C_6D_6 (only the spectral region corresponding to aliphatic protons is shown): initial spectrum (*a*); spectrum recorded during irradiation (*b*); and spectrum after photolysis (*c*) (see also Table 3).

Table 3. ^{1}H CIDNP effects in the photolysis of **1** in the presence of **5** in C_6D_6

Compound	δ	Assignment	CIDNP Effects
5	1.15 (s, 12 H),	Me	E
	1.22 (s, 12 H)		A
6	0.48 (s, 6 H)		A

The CIDNP effects recorded in the photolysis of **1** in the presence of **5** were analyzed using Kaptein's rules[20] (Eq. (1)) assuming that the *g*-factor of the germanium-centered fragment of 1,3-biradical **7** is larger than the *g*-factor of the carbon-centered fragment of this biradical and that the HFC constants of methyl protons of the germyl group are positive. In this case, absorption of molecule **6** indicates that dimethylgermylene enters the reaction with thiocycloheptyne **5** in the triplet state: $\Gamma = +$ ($\mu > 0$, $\varepsilon > 0$, $g > 0$, $a > 0$). Analysis shows that the HFC constants of positively polarized protons of the Me group of the thiocycloheptyne moiety in γ-position with respect to the paramagnetic center are negative:

Scheme 4



$\Gamma = +$ ($\mu > 0$, $\varepsilon > 0$, $g < 0$, $a < 0$). What we thus get looks as follows: the addition of (triplet) germylene to the triple bond of compound **5** results in triplet 1,3-biradical **7**, which then can (i) undergo a singlet—triplet intersystem crossing followed by the formation of adduct **6** or (ii) decompose into the initial reagents (Scheme 4). Probably, it is this situation that is characterized by negative polarization on methyl protons of the initial compound **5**: $\Gamma = -$ ($\mu > 0$, $\varepsilon < 0$, $g < 0$, $a < 0$).

It should be emphasized that this is the first reported example of the reaction of triplet Me_2Ge.[25]

3.2. Reaction with CCl_4

According to detailed analysis, the reaction of Me_2Ge with CCl_4 results in $Me_2ClGeCCl_3$, Me_2GeCl_2, and C_2Cl_6 as the main end products. In the photochemically induced reaction, the yield of the first product is at most 20 to 30%, while the yield of Me_2GeCl_2 varies between 70 and 80%.[2] In the thermally induced reaction, the yield of Me_2GeCl_2 increases up to 95%, probably due to the thermal decomposition of $Me_2ClGeCCl_3$.[11] This reaction was also studied by laser pulse photolysis and the available data on its rate constants are collected in Table 4.

CIDNP effects of methyl protons of $Me_2ClGeCCl_3$ and Me_2GeCl_2 (Table 5) were recorded in both thermal[11] and photochemical[27] decomposition of **1** in the presence of CCl_4. In addition, the photolysis of initial norbornadiene **1** was also accompanied by the observation of CIDNP effects of this compound.

Table 4. Rate constants for reaction Me_2Ge: + CCl_4 at room temperature

Precursor	Solvent	k /L mol^{-1} s^{-1}	Reference
1	C_7H_{16}	$1.2 \cdot 10^7$	2
$PhGeMe_2SiMe_3$	C_6H_{12}	$3.2 \cdot 10^8$	8
$(Me_2Ge)_6$	C_6H_{12}	$4.9 \cdot 10^8$	7

Manifestation of CIDNP effects for protons of the main products of the reaction under study means that the first stage of the reaction of dimethylgermylene with the scavenger involves a radical abstraction of a Hal atom. This results in an RP comprising the $Me_2ClGe^{\bullet}$ and $CCl_3{}^{\bullet}$ radicals. Recombination of the radicals leads to an insertion product of Me_2Ge into the C—Cl bond of the scavenger $Me_2ClGeCCl_3$. Escape of the radicals from the RP into the bulk is followed by abstraction of the second chlorine atom and results in Me_2GeCl_2 (Scheme 5). This scheme was proposed based on the analysis of the CIDNP effects observed in the photolysis of **1** in the presence of excess concentration of scavenger (see Table 5), performed according to Kaptein's rules.[20] The *g*-factor and the HFC constant of the radical $^{\bullet}GeClMe_2$ were set equal to those of trichlorogermyl radical: $g(^{\bullet}GeCl_3) = 2.0073$, the HFC constant was

Table 5. ^1H CIDNP in the thermolysis and photolysis of **1** in the presence of halogen-containing trapping agents

System **1**^{a}—trapping agent/solvent (vol.)	Reaction conditions		Reaction products	δ	CIDNP effects
	Process	T/°C			
1—CCl_4/CH_3Ph (1 : 3)	Thermolysis	80	$Me_2ClGeCCl_3$	0.80	A
			Me_2GeCl_2	0.90	E
1 (10^{-2})—CCl_4/C_6D_6 (1 : 1)	Photolysis	20	$Me_2ClGeCCl_3$	0.98^b	A
			Me_2GeCl_2	1.00^b	E
			8 ($GeMe_2$)	0.86, 0.88 (both s, 6 H)	—
1 (10^{-3})—CCl_4/C_6D_6 (1 : 3)	Photolysis	20	$Me_2ClGeCCl_3$	0.68^c	E
			Me_2GeCl_2	0.74^c	A
			$CHCl_3$	6.50	E
1—Me_3SnCl/C_6D_6	Photolysis	20	$\underline{Me_2}ClGeSnMe_3$	—	A
			$Me_2ClGeSn\underline{Me_3}$	—	A
1—$PhCH_2Br/C_6H_5Cl$	Thermal decomposition	80	$\underline{Me_2}BrGeCH_2Ph$	0.55	E
			$Me_2BrGeC\underline{H_2}Ph$	2.57	E
			Me_2GeBr_2	1.06	A
			$C\underline{H_3}Ph$	2.22	—
			$(PhC\underline{H_2})_2$	2.84	—
1—$PhCH_2Br/C_6D_{12}$	Photolysis	20	Me_2GeBr_2	0.95	A
			$PhCH_3$	2.30	—
			$(PhCH_2)_2$	2.80	—

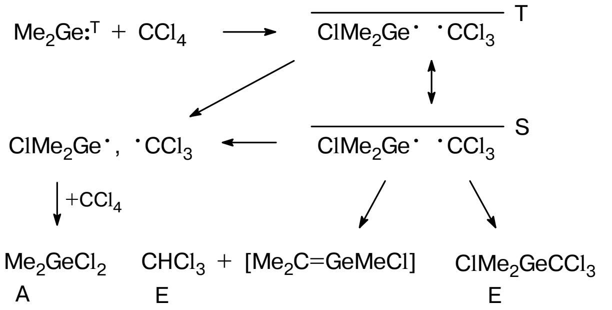
[a] The concentration of **1** (in mol L^{-1}) is given in parentheses.

[b] One line at δ_H 1.00 is observed after photolysis; the addition of Me_2GeCl_2 to the reaction mixture allows one to assign this line to methyl protons of this compound.

[c] Only one line at δ_H 0.72 corresponding to the main reaction product, Me_2GeCl_2, is observed after the reaction.

assumed to be positive by analogy with $^{\bullet}GeMe_3$, and $g(^{\bullet}CCl_3)$ was set to 2.0091.[21] Then, emission of methyl protons of the insertion product, $Me_2ClGeCCl_3$ ($\Gamma = +$, $a > 0$, $\Delta g < 0$, $\varepsilon > 0$), and absorption of Me_2GeCl_2 ($\Gamma = -$, $a > 0$, $\Delta g < 0$, $\varepsilon < 0$) correspond to $\mu > 0$, which means that the RP at issue is a triplet pair (see Scheme 5).

Scheme 5



A reaction of the triplet state of dimethylsilylene was also detected in the photolysis of 7-silanorbornadiene in the presence of high concentrations of CCl_4.[28]

An interesting fact that was reported only in the CIDNP studies[27,28] is the detection of chloroform among the products of this reaction (see Table 5). It was natural to assume that methyl protons of free radical $Me_2ClGe^{\bullet}$ serve as the source of the polarized proton of $CHCl_3$ molecule. In this case chloroform is the second cage product of the RP, which is formed as a result of the disproportionation of the RP (see Scheme 5). It is also assumed that the third product, chloromethylgermene, is formed in this process; however, attempts at detecting it in the ^1H NMR spectra failed. This is not surprising since germene derivatives containing no bulky substituents are known[3] to be reactive short-lived species.

As the concentration of initial compound **1** increases (see Table 5), the signs of the CIDNP effects for the cage and non-cage products are changed. Most likely, this is a result of the reactions of both singlet and triplet Me_2Ge. The reason can be a competition between the reactions of dimethylgermylene with CCl_4 and germanorbornadiene **1**. The latter reaction results in 7,8-digermabicyclo[2.2.2]octadiene (**8**)[13] (see Table 5).

3.3. Reaction with Me_3SnCl

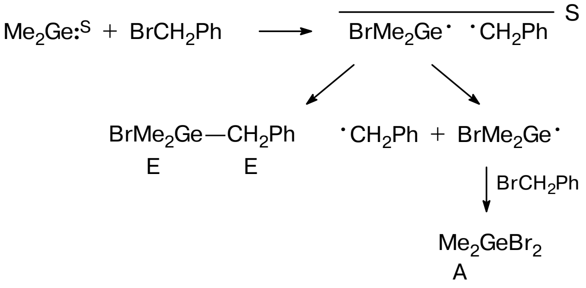
Since the rate constant of the reaction between dimethylgermylene and Me_3SnCl is rather high ($k = 3.5 \cdot 10^8$ L mol^{-1} s^{-1}),[13] one would hope that this scavenger is also capable of trapping triplet germylene. However, the polarized absorption signals of the methyl groups at the Ge and Sn atoms of the insertion product, $Me_3SnGeMe_2Cl$, detected[12] in the photoreaction of Me_2Ge with Me_3SnCl (see Table 5) cannot originate from the reaction of only singlet germylene (in this case, emission of protons of the Me_3Sn moiety should be observed). Would the reaction of triplet germylene be the main reaction channel, one would expect CIDNP effects with opposite signs, that is, E for protons at the Ge atom and A for protons at the Sn atom. Taking into account the high rate of the reaction of Me_2Ge with the scavenger, we can assume that Me_3SnCl has time to react with both states of germylene and the CIDNP effects observed are a superposition of the effects formed in both the triplet and singlet RP. This hypothesis can be confirmed or rejected only based on the analysis of the dependence of the CIDNP efficiency for $Me_3SnGeMe_2Cl$ on the concentration of Me_3SnCl. Unfortunately, no such data are available.

3.4. Reaction with benzyl bromide

The reaction of Me_2Ge with benzyl bromide was studied in detail using CIDNP technique.[11,22] It was found that the reactions of germylene generated in different manner result in different compositions of reaction products. For instance, thermally induced reaction results in $PhCH_2GeBrMe_2$ as the main product and in low yields of Me_2GeBr_2 (5%), $PhCH_3$ (5%), and $(PhCH_2)_2$ (15%).[11] Polarized proton signals of $PhCH_2GeBrMe_2$ and Me_2GeBr_2 were recorded during the reaction (see Table 5).

The CIDNP effects observed were analyzed[11,22] assuming that $g(^{\bullet}CH_2Ph) = 2.0026$, $a(^{\bullet}CH_2Ph) < 0$ (see Ref. 21), and the g-factor of radical $Me_2BrGe^{\bullet}$ is comparable in magnitude with the g-factor of trimethylgermyl radical ($g(Me_3Ge^{\bullet}) = 2.0104$). Emission of the methyl ($\Gamma = -$, $a > 0$, $\Delta g > 0$, $\varepsilon > 0$) and methylene ($\Gamma = -$, $a < 0$, $\Delta g < 0$, $\varepsilon > 0$) protons of $PhCH_2GeBrMe_2$ and absorption of Me_2GeCl_2 ($\Gamma = +$, $a > 0$, $\Delta g > 0$, $\varepsilon < 0$) indicates that Me_2Ge reacts from the singlet ground state ($\mu < 0$). The reaction mechanism is presented in Scheme 6.

Scheme 6



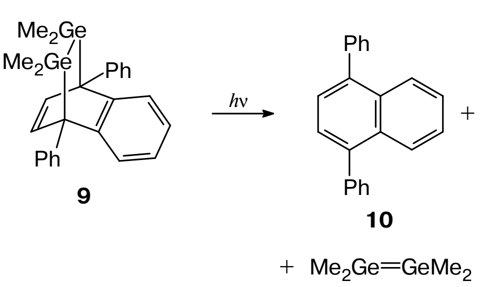
Meanwhile, only one product was found in the case of photoinitiated reaction (see Table 5). According to Scheme 6, this is a non-cage product with the same polarization as that of the thermolysis product. One can assume that both reactions proceed by the same mechanism but differ in stability of the cage product, $PhCH_2GeBrMe_2$, which is unstable under conditions of UV irradiation.

The reactions of thermally generated dimethylgermylene with CCl_3Br, $PhCH_2I$, and Ph_2CHCl also result in singlet RPs.[11]

4. Generation of digermene from 7,8-digermabicyclooctadiene

Bicyclic molecules with the bridging Ge—Ge groups are considered[3,4,17] as potential sources of digermenes, which represent another group of reactive, short-lived germanium-containing derivatives. It was suggested[29] that photochemical decomposition of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (**9**) results in 1,4-diphenylnaphthalene (**10**) and tetramethyldigermene (Scheme 7). This assumption was made based on the analysis of the end products of the reactions with trapping agents.[29]

Scheme 7

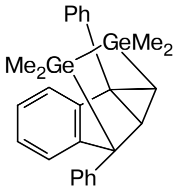


Modern concepts of the decomposition mechanisms of similar bicyclic compounds are based on analogies with the schemes proposed for germanorbornadiene derivatives.

Similarly to 7-heteronorbornadienes, the reaction mechanism was established using the experimental data on the photolysis of 7,8-digermabicyclooctadiene in solution obtained by the ^{1}H CIDNP method.[30] Studies of the photolysis of **9** allowed one to determine the composition of the end reaction products.[30,31] According to GLC and ^{1}H NMR spectroscopy data, these are compound **10**, germanium-containing oligomers including cyclic ones, and 3,4-benzo-2,5-diphenyl-6,6,7,7-tetramethyl-6,7-digermatricyclo[3.3.0$^{1.5}$.0$^{2.8}$]octane, which is a rearrangement product of the initial bicyclooctadiene **9**.

Table 6. ^{1}H CIDNP effects in the photolysis of **9** in C_6D_6

Compound	δ	Assignment	CIDNP Effects
9	0.35, 0.51 (both s)	GeMe$_2$	E
9	6.15 (s)	H(5), H(6)	E
10	7.43 (s)	H(2), H(3)	A
10	7.20—8.20 (m)	H(6—9)	—
10	7.25 (s, 10H)	Ph	—



Experiments in different solvents (C_6D_6, C_6D_{12}, a C_6D_6—CCl_4 mixture) led to observation of polarized signals from the methyl and 5,6-aromatic protons of compound **9** and from the phenyl protons of 1,4-diphenylnaphthalene (Table 6, Fig. 3).

Comparison of the data listed in Tables 2 and 6 shows that the CIDNP effects observed for compound **9** are identical to those recorded in the photodecomposition of compound **1**. Similarly to the case of the latter compound, manifestation of CIDNP effects with opposite signs for the initial compound **9** and protons of the non-cage product **10** is most likely due to the fact that these effects are formed by the S—T_0 mechanism. Thus, the results of CIDNP experiments confirm the known hypothesis that photolytic decomposition of bridging compounds containing more than one Ge follows a mechanism similar to that proposed for monogermanium analogs, *i.e.*, *via* cleavage of one of the endocyclic C—Ge bonds and intermediate formation of 1,6-biradical **11**.

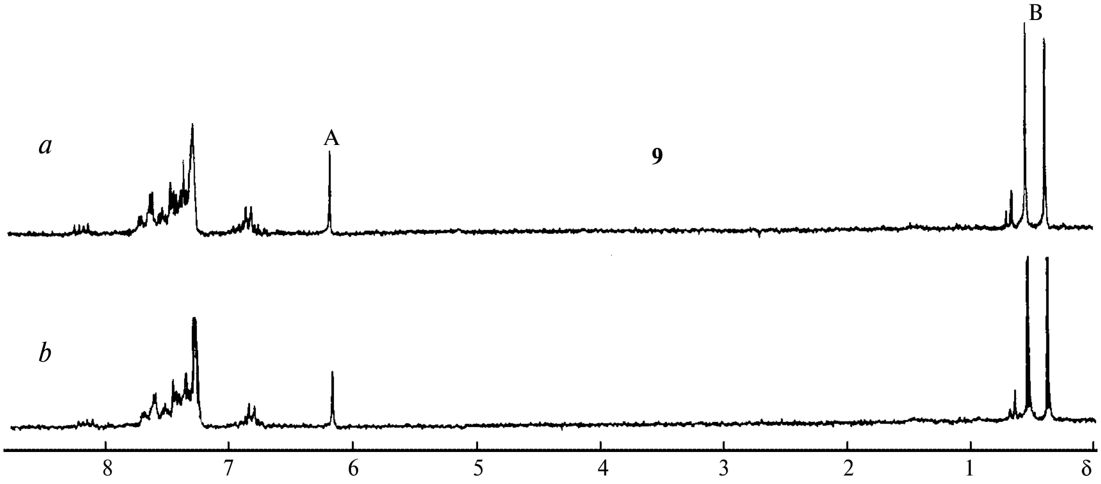
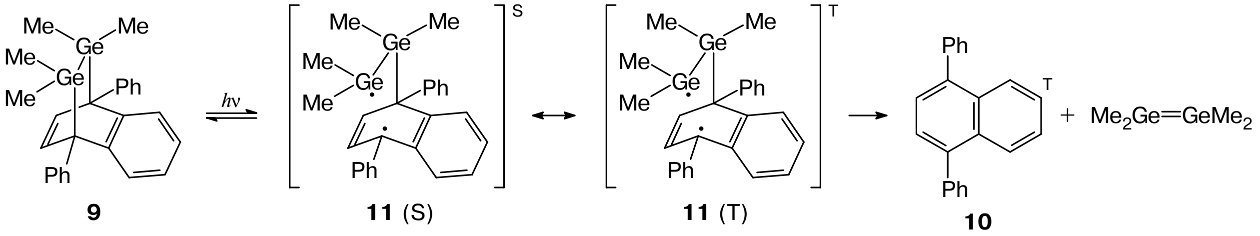


Fig. 3. ^{1}H CIDNP effects in the photolysis of **9** in C_6D_6: initial spectrum (*a*) and spectrum recorded during photolysis (*b*) (see also Table 6). The signals of C(5)H and C(6)H are labeled by A and the signals of GeMe$_2$ are labeled by B.

Scheme 8



The CIDNP effects observed were analyzed[30] using Kaptein's rules[20] (Eq. (1)). The assumptions of the magnetic resonance parameters of 1,6-biradical **11** were as follows: the *g*-factor of the germanium-centered fragment is larger than that of the carbon-centered moiety and the HFC constant on methyl protons is positive. The results of analysis showed that the initial digermabicyclooctadiene **9** regenerates *via* recombination of the singlet state of 1,6-biradical **11** ($\Gamma = -$, $\mu < 0$, $\varepsilon > 0$, $a > 0$, $\Delta g > 0$), whereas the triplet state of biradical **11** decomposes, by analogy with Scheme 3, *via* cleavage of the second Ge—C bond to give 1,4-diphenylnaphthalene in the triplet excited state ($\Gamma = +$, $\mu > 0$, $\varepsilon < 0$, $a > 0$, $\Delta g < 0$) and tetramethyldigermene (Scheme 8).

The formation of a compound in the triplet excited state from triplet 1,6-biradical **11** follows from the total spin conservation rule. In this case, the excitation should be ascribed to diphenylnaphthalene, which was confirmed by laser pulse photolysis.[30,31] Indeed, photolysis of a solution of **9** leads to the appearance of an intense absorption band with a characteristic maximum at $\lambda = 420$ nm in hexane[30] and at $\lambda = 430$ nm in cyclohexane[31] immediately after the first laser pulse. This band is rapidly quenched in the presence of O_2 ($k_{\text{quench}} = 3.5 \cdot 10^9$ L mol^{-1} s^{-1}). The results obtained are in good agreement with the known data on the T—T absorption of compound **10**,[32] and this allowed the authors to assign the observed absorption band to the triplet excited state of **10**. This fact serves as a confirmation of Scheme 8 that was proposed based on the analysis of CIDNP effects.

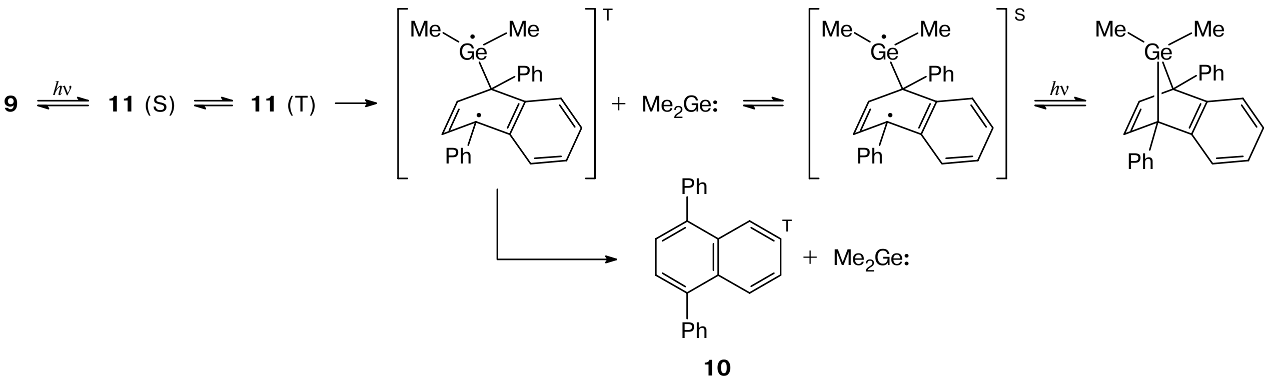
Meanwhile, attempts at using a laser with $\lambda = 308$ nm as a source of exciting light to detect a signal at $\lambda = 380$ nm failed (this signal was found using exciting light at $\lambda = 266$ nm and assigned[31] to tetramethyldigermene). Different results of the studies[30,31] can be explained by relatively low yield of digermene in the generation procedure[30] due to substantial difference in the extinction coefficients of compound **9** in the spectral regions in question.

However, the results presented above do not allow one to decide unambiguously that the decomposition of compound **9** according to Scheme 8 is the only possible mechanism. Meanwhile, a concurrent reaction involving successive generation of two germylene molecules (see Scheme 9) cannot be ruled out.

The latter mechanism a cleavage of the Ge—Ge rather than Ge—C bond in 1,6-biradical **11**. The newly formed 1,5-biradical can follow two alternative reaction pathways, (i) recombination to give germanorbornadiene and (ii) cleavage of the second Ge—C bond with the formation of **10** and generation of the second germylene molecule. The mechanism (ii) implies the formation of digermene as a result of dimerization of germylenes and is rather common in the literature on the subject.[1,3,4]

Would the reaction follows this mechanism, one can expect the appearance of polarized NMR signals from germanorbornadiene; however, attempts at detecting them in CIDNP experiments failed.[30] Nevertheless, this does not mean that no dimethylgermylene is formed in this reaction since, first, no accumulation of germanorbornadiene can probably occur under condi-

Scheme 9



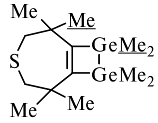
tions of steady-state UV irradiation and, second, germylene—digermene interconversions can occur in solutions. Such interconversions have been much studied for the so-called Lappert's digermene derivatives with hydrocarbon substituents, *e.g.*, $(Me_3Si)_2CH$. These compounds undergo a spontaneous dissociation into germylenes in solution or in the gas phase, so their further reactions with various trapping agents result in solely monogermanium derivatives.[3,4] According to calculations,[1] this is also possible for the simplest digermenes.

It was a reasonable continuation of investigations of the phototransformation mechanisms of compound **9** to study them in the presence of scavengers capable of entering the reactions with postulated intermediates (germylene and digermene).[30] Using this research strategy and comparing the CIDNP effects detected in the photolysis of **1** and **9** in the presence of trapping agents, the formation mechanisms of tetramethyldigermene and dimethylgermylene from compound **9** were studied and the spin states of carbenoids that (i) were newly formed in the reactions under study and (ii) enter the reactions with scavengers were determined.

5. Reactions of intermediates formed in the photolysis of 9 in the bulk

It seems to be useful to begin our consideration with the transformations occurring in the photolysis of compound **9** in the presence of trapping agents containing multiple bonds, since digermene is known to undergo insertion into these bonds.[3,4] In particular, similarly to germylene, tetramethyldigermene can insert into the triple bond of thiocycloheptyne to give digermacyclobutene.[33] It is convenient to compare the results of CIDNP studies of the photolysis of compounds **1** and **9**, thus revealing (possible) similarity and distinctions between the intermediates formed in these phototransformations.

Table 7. ^1H CIDNP effects in the photolysis of **9** in the presence of **5** in C_6D_6

Compound	δ	Assignment	CIDNP Effects
5	1.15 (s, 12H)	Me	E
6	1.22 (s, 12H)	Me	A
6	0.48 (s, 6H)	$GeMe_2$	A
	1.13 (s, 12H)		A
	0.88 (s, 12H)	Me	—

The data on the CIDNP effects recorded during the photolysis of compound **1** in the presence of **5** are listed in Table 3. Photolysis of **9** is also accompanied by the observation of polarized signals in the ^1H NMR spectrum (Table 7, Fig. 4).

Two of them (at δ_H 1.22 and 0.48) match the signals assigned to product **6** that was formed in the insertion of dimethylgermylene into the triple bond of thiocycloheptyne **5** (see Table 3). Additional signals (at δ_H 1.13 and 0.65) recorded in this system can be assigned to an adduct of digermene with thiocycloheptyne.[33] The signal at δ_H 1.13 was assigned to Me groups of the thiocycloheptyne fragment of this adduct, while the signals at δ_H 0.65 were assigned to methyl groups at Ge

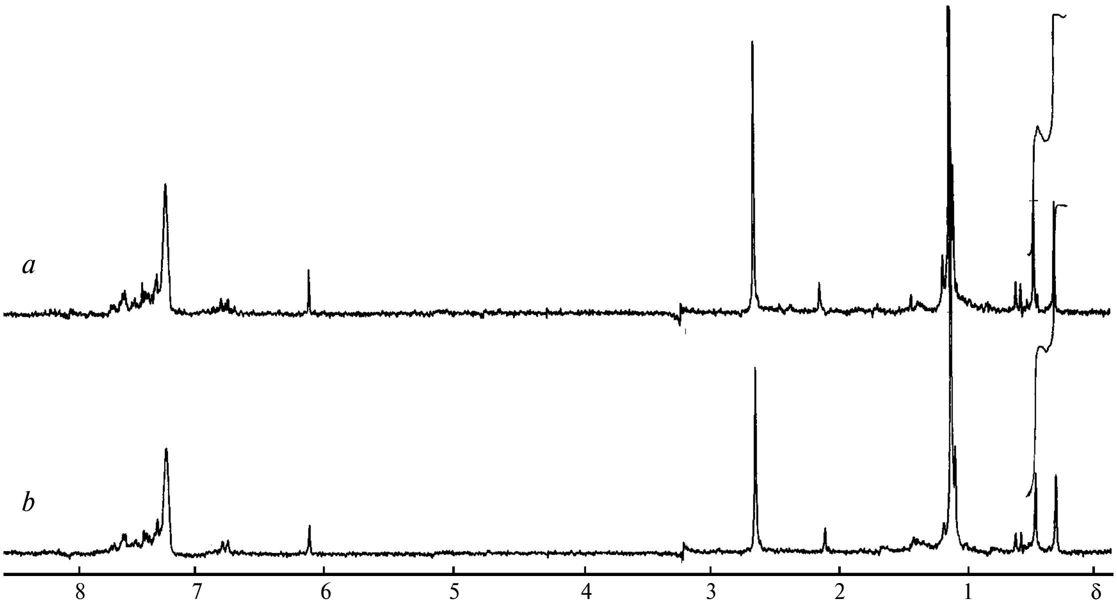


Fig. 4. ^1H CIDNP effects observed in the photolysis of **9** in the presence of **5** in C_6D_6: spectrum recorded during irradiation (*a*) and spectrum after photolysis (*b*) (see also Table 7).

atoms. Both groups of signals exhibit weak positive polarization (see Fig. 4).

Signals from the cyclobutene adduct are accumulated only in the initial stage of the photolysis of **9**. Judging from the NMR spectrum, long-term exposure of the sample to UV irradiation leads to germacyclopropene **6** as the main product (see Fig. 4). This is an indication of the low stability of digermabicyclobutene derivative under conditions of steady-state photolysis. Photodecomposition of this derivative can result in the formation of germylene and corresponding germacyclopropene. Yet another route of formation of polarized germacyclopropene adduct consists in the above-mentioned insertion of triplet dimethylgermylene into the triple bond of thiacycloheptyne, which involves a biradical stage (see Scheme 4). The main problem is correct determination of the source of triplet germylene in the system under study, which requires making a decision between the decomposition of germacyclobutene an tetramethyldigermene. As mentioned above, interconversion of digermene and germylene derivatives including spontaneous decomposition of the former is rather common in the literature on the subject.[3,4] It is also believed that the double bond in digermene derivatives is not a true double bond owing to weak side overlap of the p-orbitals of electrons of the Ge atoms.[3,4] This does not exclude the possibility for both singlet and triplet germylene to be formed in the decomposition of digermene (Scheme 10).

Scheme 10

$$\mathrm{Me_2Ge{=}GeMe_2} \longrightarrow \mathrm{Me_2Ge{:}^{S}} + {}^{\mathrm{T}}\mathrm{{:}GeMe_2}$$

In any case, the fact that the CIDNP effects recorded in the photolysis of compounds **1** and **9** in the presence of thiocycloheptyne **5** for the cyclopropene adduct **6** follow the same pattern confirms that both reactions proceed with participation of triplet dimethylgermylene. In addition, manifestation of CIDNP effects of methyl groups of the cyclobutene adduct suggests that the formation mechanism of this adduct is similar to that presented in Scheme 4, but involves a stage with participation of 1,3-biradical. To assess the possibility for germylene to be generated from digermene and to study the distinctions in the reactivity of these two short-lived species, it is useful to compare the CIDNP effects recorded in the reactions with halogen-containing scavengers.

Previously, we found that compound **9** spontaneously reacts with CCl_4 and $PhCH_2Br$ at room temperature and that these thermally induced reactions are slow and do not preclude the observation of CIDNP effects in the photolysis. In addition, the presence of these trapping agents presents no obstacles to manifestation of the CIDNP effects observed in the photolysis of initial compound **9**. This means that the scavengers do not react with the intermediate 1,6-biradical **11** in which CIDNP effects are formed (see Scheme 8, Table 8).

Table 8. ^{1}H CIDNP effects in the photolysis of **9** in the presence of alkyl halides

System	Products	δ (*J*/Hz)	CIDNP Effects
9—CCl_4/C_6D_6	$Me_2ClGeCCl_3$	0.67	E (w)
(1 : 3)	Me_2GeCl_2	0.70	A (w)
	$CHCl_3$	6.45	E
9—$PhCH_2Br/C_6D_6$	Me_2GeBr_2	1.10	E
	Intermediates	4.30	E
		3.50 (dd, *J* = 7.0; *J* = 4.0)	A
		5.20 (t, *J* = 7.0)	E

In addition to studies of CIDNP effects, the photoinduced reaction of **9** with CCl_4 was studied[31] and the following reaction products were identified (the yields are given in parentheses as fractions of the stoichiometric composition): **2** (95%), C_2Cl_6 (37%), $ClMe_2GeGeMe_2Cl$ (71%), and Me_2GeCl_2 (27%).[31] Considerable amount of dichlorotetramethyldigermane found among the reaction products was explained[31] by successive abstraction of chlorine atoms from two scavenger molecules by digermene; however, this product can also be formed as a result of germylene insertion into the Ge—Cl bond of Me_2GeCl_2.[11]

Meanwhile, the presence of the known[31] and newly found monogermanium reaction products and polarized chloroform indicates that dimethylgermylene is also involved in the reaction (*cf.* Tables 4 and 8). It should be noted that rather strong polarization with the same sign as and in the photolysis of **1** was observed only for $CHCl_3$, whereas the methyl protons of $Me_2ClGeCCl_3$ and Me_2GeCl_2 are rather weakly polarized. Superposition of the lines from methyl groups of dichlorotetramethylgermane and products of the dark reaction of compound **9** with CCl_4 on the signals of these products additionally hampers the observation of CIDNP effects.

Thus, the fact that photolysis of **9** in the presence of CCl_4 results in (i) the same monogermanium compounds as the reaction of germanorbornadiene **1** does and (ii) polarized chloroform points to the formation of dimethylgermylene, which enters the reaction with CCl_4 in the triplet state (see Scheme 5). However, the reaction of dimethylgermylene in the singlet ground state cannot also be ruled out. This reaction can be suggested based on the weak polarization on methyl protons of $Me_2ClGeCCl_3$ and Me_2GeCl_2. Triplet Me_2Ge can be formed in the photodecomposition of **9** as a result of the decomposition of digermene into two germylene molecules, one of which is in the triplet state (see Scheme 10). In fact, CIDNP studies of this system revealed only the reaction of dimethylgermylene with CCl_4; digermene did not manifest itself in the presence of CCl_4 despite the rather high rate constant for this reaction ($k = 1.2 \cdot 10^7$ L mol^{-1} s^{-1}) obtained from laser pulse photolysis experiments.[31]

The reverse is observed in the photolysis of 7,8-digermabicyclooctadiene **9** in the presence of benzyl bromide. Comparison of the CIDNP effects recorded during the phototransformations of **1** and **9** in the presence of $PhCH_2Br$ reveals marked distinctions (see Tables 5 and 8).

Photolyses of both compounds, **1** and **9**, in the presence of benzyl bromide result in dibromodimethylgermane. Similarly to dichlorodimethylgermane that is formed in the photolysis of **9** in the presence of CCl_4 (see Table 8), dibromogermane is also polarized, which suggests that it was formed in the reaction of triplet germylene.

The most important distinction between these systems is the presence of polarized signals in the spectral region near the signals of methylene protons of the scavenger (at δ_H 4.30) and in the double bond region (Fig. 5). The observed pattern of CIDNP effects allows one to draw some definite conclusions. First, positions of the polarized signals indicate that the intermediates generated in the photolysis of **9** react with the trapping agent *via* insertion into the benzene ring followed by the aromatic ring opening rather than into the C—Br bond (which is typical of germylene reactions). Insertion of digermene and disilene into the double bonds of aromatic molecules (anthracene, benzene derivatives, heterocycles) to give the corresponding bicyclic compounds was reported.[3,4] However, no similar reactions of germylene and silylene derivatives with benzene and naphthalene were found.[1,2] Therefore, the assumption that it is tetramethyldigermene that reacts with benzyl bromide to produce the CIDNP effects observed seems to be well substantiated. However, the reaction products are unstable and cannot be accumulated in the course of photolysis. Mass spectrometric analysis of the reaction mixture only allows the detection of dibromodimethylgermane, dibenzyl, and oligogermanes.[31] Therefore, the only source of information on these unstable products are polarized signals. The pattern of the NMR spectrum (see Fig. 5) suggests that the polarized signals (a triplet at δ_H 5.0 with $J = 7$ Hz and a doublet of doublets at δ_H 3.50 with $J = 7$ and $J = 4$ Hz) cannot be assigned to one compound, in particular, because of the absence of a signal with $J = 4$ Hz. Most likely, the NMR spectrum represents a superposition of polarized signals from several short-lived diamagnetic intermediates. Signals from other protons are not observed due to their superposition or small CIDNP coefficient. It should be noted that the known[3,4] insertion products of digermene are, as a rule, 1,4-bicyclic derivatives. In the spectral region in question, they should exhibit the following NMR spectral pattern: a triplet from proton in *para*-position (with respect to the methylene bromide fragment), a triplet of doublets from protons in *ortho*-position, a doublet of doublets from protons in *meta*-position, and a singlet from protons of the methylene bromide fragment. It is reasonable to assume that Fig. 5 presents only a part of the NMR spectrum. Probably, the newly formed 1-bromomethyl-7′,7′,8′,8′-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene decomposes upon irradiation with light with successive elimination of two dimethylgermylenes and regeneration of benzyl bromide.

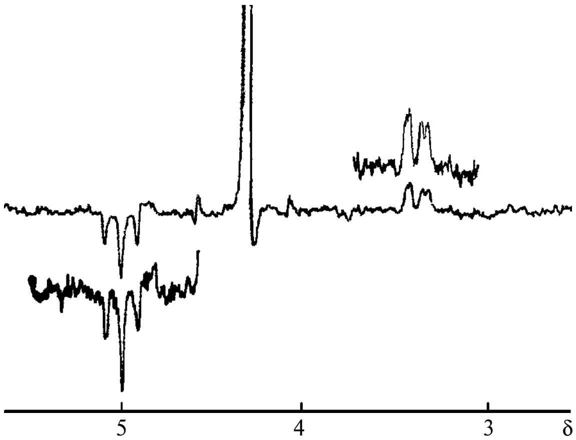


Fig. 5. ^1H CIDNP effects in the photolysis of **9** in the presence of benzyl bromide in C_6D_6 (see also Table 8).

In this case, the absence of analogous CIDNP effects in the photolysis of **1** (here, digermene can be obtained only by dimerization of germylene) and manifestation of the reactions typical of germylene is evidence for the generation of germylene in the photolysis of **9** *via* decomposition of digermene (see Scheme 10).

Thus, studies of the reactions with trapping agents in the photolysis of **9** allows one to distinguish between the reactions of digermene and germylene and to draw definite conclusions about the reactivity of these intermediates.

6. Conclusion

The results presented in this review show the potentialities of spin chemistry methods for detailed elucidation of the role of organometallic intermediates containing germanium atoms (germylene, digermene, and substituted germyl free radicals) in various chemical reactions. In particular, they make it possible to establish the biradical and free-radical stages in the reaction under study and to determine the spin states from which paramagnetic intermediates react. The combination of CIDNP and kinetic methods allowed one to gain a better insight into the chemistry of divalent germanium derivatives.

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