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ABOUT THE MECHANISM OF THE PHOTOLYSIS OF BENZOYLTRIETHYLGERMANE, $Et_3GeCOPh$

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Summary

The detailed mechanism of the photolysis of benzoyltriethylgermane $Et_3GeCOPh$ in various media has been studied using the chemically induced dynamic nuclear polarization method (^1H CIDNP). It has been shown that in all cases the photolytic decomposition leads to the formation of the initial triplet radical pair (RP) of $Et_3\dot{G}e$ and $Ph\dot{C}O$.

Introduction

The reactivity and photochemical reactions of the organometallic ketones containing Group IV elements (Si and Ge) were systematically studied by Brook et al. (see, e.g., [1–4]). In particular, they found that the photolysis of α-metal containing ketones leads to either Norrish Type 1 cleavage, or the formation of various carbenes (siloxy- or germoxycarbenes). It has been shown [1–4], that the mechanism of the photodecomposition of these ketones strongly depends on the polarity and nature of the solvent.

The appearance of the element-centered free radicals in these processes is confirmed by the use of chemically induced dynamic nuclear polarization of protons (^1H CIDNP) [5,6]. In particular, it has been shown that the primary act of the photodecomposition of benzoyltriethylgermane $Et_3GeCOPh$ is the formation of the radical pair (RP) of benzoyl ($Ph\dot{C}O$) and triethylgermyl ($Et_3\dot{G}e$) free radicals [6].

The present paper is devoted to the clarification of the detailed mechanism of the photolysis of benzoyltriethylgermane $Et_3GeCOPh$ in C_6D_6, cyclo-C_6D_{12} in the presence of the radical traps $PhCH_2Cl$ and CD_3OD, and in the absence of them by use of the ^1H CIDNP method.

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Experimental

Benzyl chloride $PhCH_2Cl$ was purified by vacuum distillation (61.5 °C, 10 mmHg). Benzoyltriethylgermane was synthesized by a published method [7] and was purified by preparative GLC. All deuterated solvents (C_6D_6, cyclo-C_6D_{12}, CD_3OD, toluene-d_8 (V/O "Izotop")) were used without additional purification. The reaction mixtures of benzoyltriethylgermane $Et_3GeCOPh$ (0.05–0.15 M) in C_6D_6, cyclo-C_6D_{12} with the traps: $PhCH_2Cl$ (0.4–2 M), CD_3OD (0.4–2 M) or without them were irradiated directly by the full light of a super high pressure mercury lamp DRSh-1000 (1 kW) in the probe of a Tesla BS 487C NMR spectrometer (80 MHz). A thermal filter was used to prevent heating of the sample.

To analyze the products of reactions a Varian XL-200 NMR spectrometer (200 MHz) and a Varian GC/MS MAT 212 (J_{ion} 70 eV) were used.

To study the radical-adducts a Bruker ER-200D-SRC ESR spectrometer (X-range) was used. Solutions of $Et_3GeCOPh$ in toluene-d_8 0.05–0.15 M were irradiated by the full light of super high pressure mercury lamp DRSh-500 (500 W) at −20 °C whereupon the ESR spectra were recorded.

To analyze the CIDNP effects employing the existing rules [8], we used g-factor values and *hfi* constants of free radicals from [9]: $g(\mathrm{Et_3\dot{G}e}) = 2.0089$; $a(\mathrm{CH_2}) \leqslant 0.5$ mT; $g(\mathrm{Ph\dot{C}O}) = 2.0008$.

Results and discussion

Figure 1 shows the ^1H CIDNP effects which arise during the photolysis of benzoyltriethylgermane $Et_3GeCOPh$ in C_6D_6 and cyclo-C_6D_{12} in the presence of benzyl chloride $PhCH_2Cl$. Note, that the PMR spectrum of the triethyl fragment of $Et_3GeCOPh$ is an example of an A_3B_2 spin system in which the protons of groups A and B are magnetically equivalent, thus the PMR spectrum of this fragment is a singlet. The strong emission signal (Fig. 1b) at δ 0.9 ppm, is related to the triethyl group of chlorotriethylgermane Et_3GeCl; the enhanced absorption δ ~ 1 ppm is related to the analogous protons of the initial benzoyltriethylgermane, and the emission at δ 3.8 ppm is related by chemical shift to the α-CH_2 protons of benzylphenyl ketone $PhCH_2COPh$. The ^1H CIDNP effects which arise during photolysis of $Et_3GeCOPh$ are listed in Table 1. The analysis of the CIDNP effects of the ethyl protons of the ketone and chlorotriethylgermane shows that they arise as effects in the "in-cage" product and the product in the bulk from the triplet RP of $\mathrm{Ph\dot{C}O}$ and $\mathrm{Et_3\dot{G}e}$ free radicals, respectively. The conclusion about the multiplicity of the initial RP is confirmed by the CIDNP effects observed during the photolysis of benzoyltriethylgermane in the absence of radical traps. In this case, the absorption of the ethyl protons of the ketone is also observed (Fig. 2, Table 1).

The emission of the α-CH_2 group of benzylphenyl ketone ($PhCH_2COPh$) during the photolysis of $Et_3GeCOPh$ in the presence of $PhCH_2Cl$ can arise both during the recombination of the benzyl and benzoyl radicals in the bulk (F-pair), and during the possible photodecomposition of $PhCH_2COPh$ (back-recombination of the triplet radical pair: $\overline{\mathrm{Ph\dot{C}H_2\,\dot{C}OPh}}^{T}$). Note, that in the framework of the CIDNP effects analysis these situations are indistinguishable.

Previous studies of the photolyses of α-element-containing ketones without the radical traps [4] have shown that the element-centered radicals generated usually

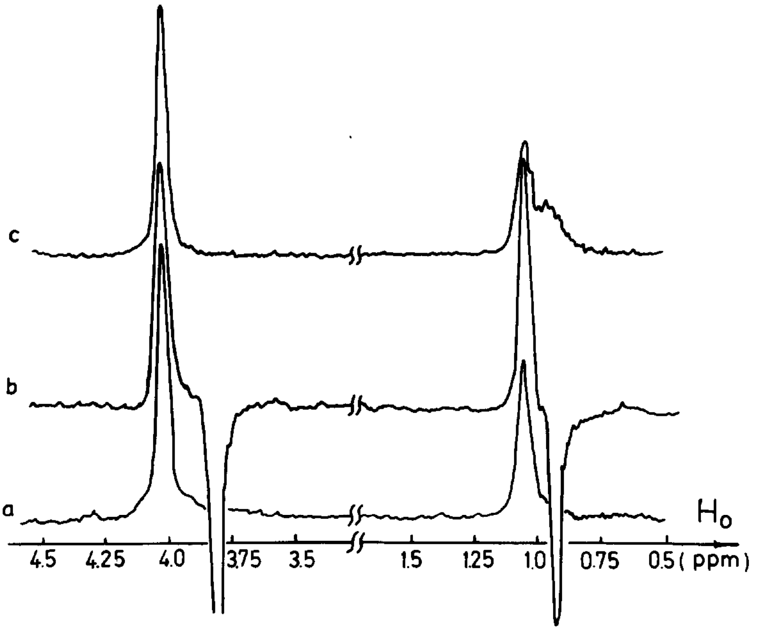


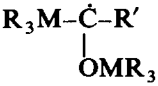
Fig. 1. ^1H CIDNP effects observed during the photolysis of $Et_3GeCOPh$ in the presence of $PhCH_2Cl$ ($Et_3GeCOPh$: $PhCH_2Cl = 1:3$) in C_6D_6: (a) before reaction; (b) during UV-irradiation; (c) after reaction.

TABLE 1

^1H CIDNP EFFECTS DURING THE PHOTOLYSIS OF BENZOYLTRIETHYLGERMANE $Et_3GeCOPh$ IN C_6D_6 AND cyclo-C_6D_{12} (A = absorption, E = emission).

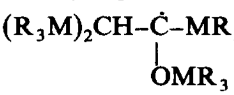
Trap	Main products	^1H CIDNP effects
$PhCH_2Cl$	$Et_3GeCOPh$	A (ethyl protons)
	Et_3GeCl	E (ethyl protons)
	$PhCH_2COPh$	E (α-CH_2 group)
CD_3OD	$Et_3GeCOPh$	A (ethyl protons)
	$Et_3GeOCD(OCD_3)Ph$	E (ethyl protons)
–	$Et_3GeCOPh$	A (ethyl protons)

attack the most electronegative atom of the initial ketone, in this case the oxygen atom of the carbonyl group. Indeed, recently it was demonstrated that α-element-containing ketones are very effective traps for the element-centered radicals of type $R_3\dot{M}$ (M = Si, Ge) [10]. The resulting radical-adducts



$$R_3M\text{-}\underset{\displaystyle OMR_3}{\underset{|}{\dot{C}}}\text{-}R'$$

lead to the great number of products through disproportionation reactions. Among the acylorganosilanes (-germanes) are rather stable radicals



$$(R_3M)_2CH\text{-}\underset{\displaystyle OMR_3}{\underset{|}{\dot{C}}}\text{-}MR_3,$$

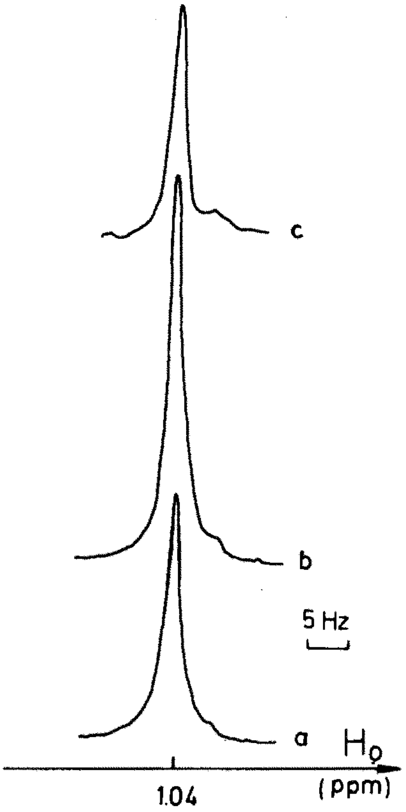
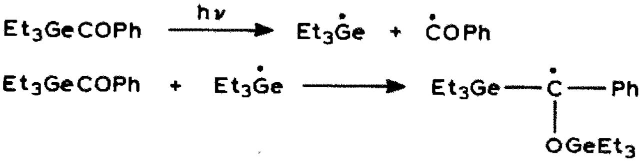


Fig. 2. The photolysis of $Et_3GeCOPh$ in C_6D_6: (a) before photolysis; (b) during photochemical reaction; (c) after reaction.

the structure of which has been confirmed by ESR spectroscopy [10].

To examine the likely formation of the adducts in the reactions under study we also recorded the ESR spectra of the irradiated solutions of benzoyltriethylgermane in toluene-d_8. The samples were irradiated during 15 min at −20 °C and then transferred to the resonator of the ESR spectrometer. Broadening of the spectrum at 0 °C was observed (Fig. 3). The sample was left in the resonator for 30 min at 0 °C, during which the spectrum was resolved (Fig. 4). The approximate value of the g-factor (Fig. 4) was 2.0033. From the data in ref. 10 one can assume that this spectrum is due to the protons of a phenyl ring, thus it can also be ascribed to the radical-adduct I (see eqs. 1).



$$\begin{gathered} Et_3GeCOPh \xrightarrow{h\nu} Et_3\dot{G}e + \dot{C}OPh \\ Et_3GeCOPh + Et_3\dot{G}e \longrightarrow Et_3Ge-\overset{\bullet}{\underset{OGeEt_3}{C}}-Ph \end{gathered} \qquad (1)$$

(I)

However, in contrast to the radical-adducts described in ref. 10, there is no signal

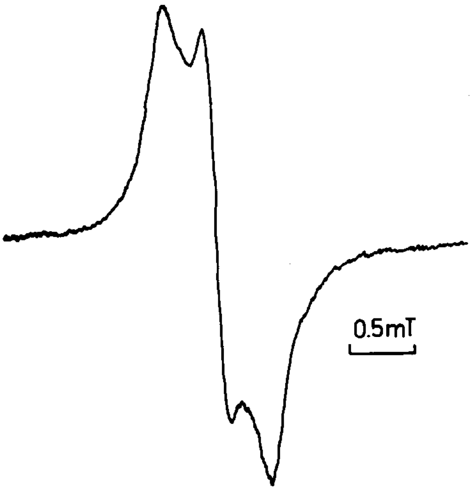
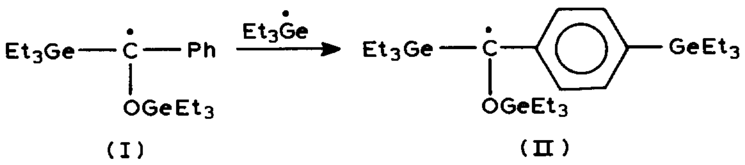


Fig. 3. The ESR spectrum of the radical resulting from the irradiation of $Et_3GeCOPh$ in toluene-d_8 at −20 ° C. The spectrum was taken at the first moment after the sample transfer to the resonator of ESR spectrometer (the registration was performed at 0 ° C).

from the *para*-protons of the ring in this case. The characteristic picture - a triplet of triplets (a(*ortho*) = 0.426 mT, a(*meta*) = 0.16 mT) can be attributed to the following structure (II) (see eq. 2).



(2)

The formation of such a radical (II) may be directed by steric hindrances preventing

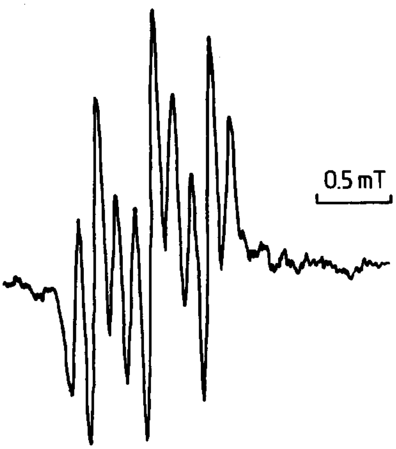
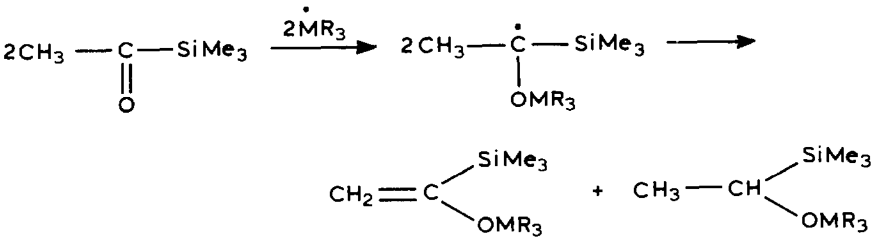


Fig. 4. The same as in Fig. 3 after 30 min at 0 ° C in the resonator of ESR spectrometer.

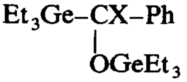
attack on the aliphatic α-carbon atom and also by the unlikely occurence of disproportionation as shown by the acylorganosilanes [10] (eq. 3)



(3)

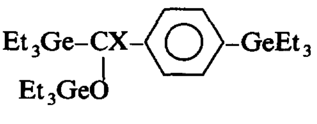
(M = Si, Ge)

Thus, in contrast to the experiments by Brook et al. [1] on the photolysis of α-element-containing ketones in CCl_4, chlorotriethylgermane (Et_3GeCl, the product of the abstraction of chlorine atom by the element-centered radical from the radical trap, $PhCH_2Cl$) is not the sole germanium-containing product in our experiments. This is confirmed by the results of the investigation of the kinetic parameters of the various reactions of $R_3\dot{G}e$ radicals, carried out by Ingold et al. [11]. It has been shown that the bimolecular rate constant of chlorine abstraction from benzyl chloride by the germanium-centered radical is 10–100 times smaller than the absolute rate constant of the addition of this radical to some carbonyl compounds. Whereas the rate constant for the chlorine abstraction from CCl_4 is of the same order as that for addition to ketones. This is in good agreement with the conclusion of Alberti et al. [10], that α-element-containing ketones are the most efficient traps for self-generated radicals during the photolytic reactions of $R_3\dot{M}$ (M = Si, Ge) free radicals. Indeed, NMR spectroscopy and GC/MS investigations of the products of $Et_3GeCOPh$ photolysis both in the presence of benzyl chloride and without it, have shown that in addition to Et_3GeCl the reaction mixture contains phenyltriethylgermane Et_3GePh, which is formed as a result of decarbonylation in the RP of $Et_3\dot{G}e$ and $Ph\dot{C}O$ (see Scheme 1), and also the products of the decay of radical-adducts I and II:



$Et_3Ge{-}CX(OGeEt_3){-}Ph$

and



(where X = Cl, H, D – for different initial reaction mixtures). Quantitative analysis of the reaction products, even by use of GC/MS was unsuccessful. This fact is connected with the inability of GC to separate the adducts I and II (i.e., the products of their decay), thus their structures were assigned from their ESR and NMR spectra. Thus, the $Et_3\dot{G}e$ radical released takes part in two competitive reactions; (i) the abstraction of the chlorine from $PhCH_2Cl$; and (ii) the addition to

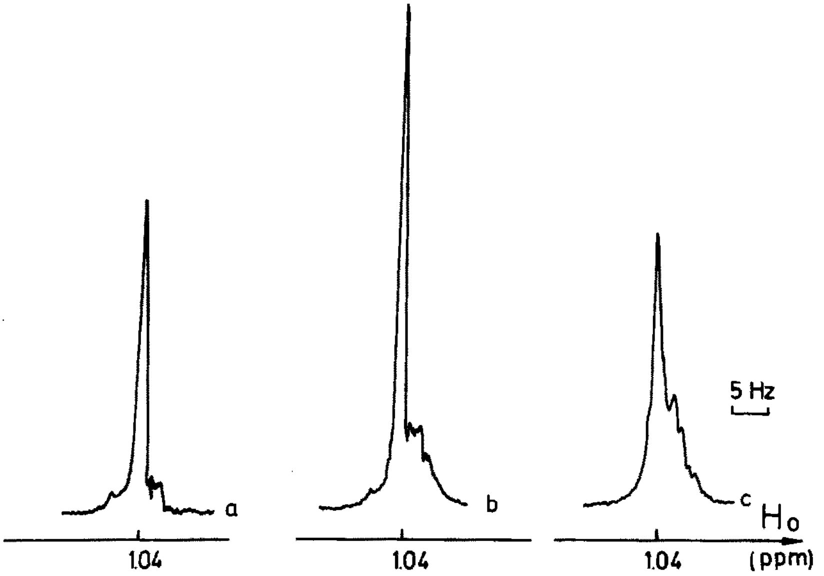


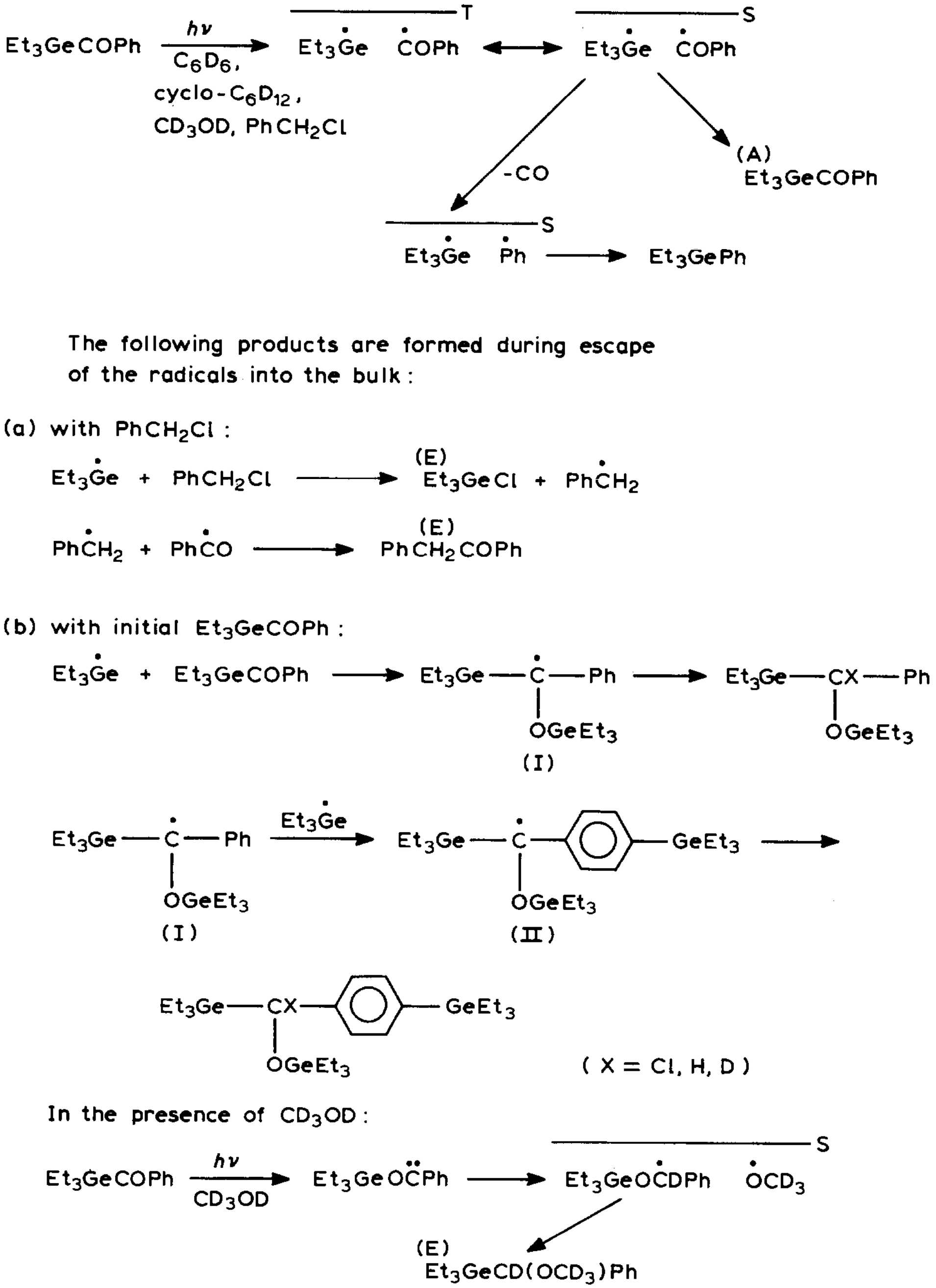
Fig. 5. ^{1}H CIDNP effects of the ethyl protons of benzoyltriethylgermane during the photolysis of $Et_3GeCOPh$ in the presence of CD_3OD ($Et_3GeCOPh$: CD_3OD = 1 : 1) in C_6D_6: (a) before photochemical reaction; (b) during UV-irradiation; (c) after reaction.

the C=O bond of the initial $Et_3GeCOPh$. Since both processes are bimolecular, the contribution of each depends on the relationship between the concentrations of $PhCH_2Cl$ and $Et_3GeCOPh$ ($K_{abstr}/K_{add} \approx 0.01$–$0.1$ [11]).

Photolysis of the α-element-containing ketones in alcohol seemed not to involve the Norrish Type 1 cleavage stage, i.e. the element-centered radicals were thought not to take part in these reactions [3]. Nevertheless, it was possible to identify the various stages and radicals formed during the photodecomposition of $Et_3GeCOPh$ in methanol.

The ^{1}H CIDNP effects observed for the ethyl protons of the initial $Et_3GeCOPh$ during the photolysis in the presence of CD_3OD are shown in Fig. 5. The absorption observed in the ethyl protons of the initial ketone indicates that the photolysis of benzoyltriethylgermane in the presence of CD_3OD, as in the previous cases, includes the initial triplet RP of $Et_3\dot{G}e$ and $Ph\dot{C}O$ (Table 1). However, this result does not exclude the possible formation of the germoxycarbene intermediate, which has been previously described [2,3]. The emission signal was observed at δ 1.1 ppm. From its chemical shift this signal can be assigned to the ethyl group of the mixed acetal, $Et_3GeOCD(OCD_3)Ph$. The data obtained by Brook et al. [2,3] show that such products formed are due to the insertion of germoxycarbene into the O–H bond of the methanol molecule. The presence of the emission of the ethyl protons of the acetal indicates that this product is formed in a singlet RP (See Scheme 1). It is likely that during the photolysis of the ketone in a polar medium (methanol), both routes of the reaction are followed: i.e. photodecomposition through Norrish Type 1 cleavage, and the formation of germoxycarbene.

The experimental facts described above allowed us to propose a scheme showing the various stages and radicals formed during the photolysis of $Et_3GeCOPh$ in various media (Scheme 1).



SCHEME 1. The mechanisms of the formation of ^1H CIDNP effects during the photolysis of $Et_3GeCOPh$ in various media (T and S are multiplicities of RPs, A and E – the absorption and emission, respectively).

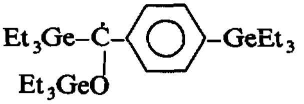
Only small amounts of the following compounds: PhCl, PhCOCl, Et_3GeCH_2Ph, $PhCH_2CH_2Ph$, $Et_3GeGeEt_3$ were detected among the reaction products after NMR and GC/MS studies.

Conclusions

(1) The presence of the radical stages in the photolysis of benzoyltriethylgermane $Et_3GeCOPh$ in C_6D_6, cyclo-C_6D_{12} with the radical traps $PhCH_2Cl$ and CD_3OD and without them was demonstrated using ^1H CIDNP method.

(2) It has been shown that in all cases the photolysis of $Et_3GeCOPh$ leads to the formation of the initial triplet radical pair of $Et_3\dot{G}e$ and $Ph\dot{C}O$.

(3) It has been found that the photolysis of $Et_3GeCOPh$ without a trap leads to the formation of a stable radical with hypothetical structure



($g \sim 2.0033$; $a\,(ortho) = 0.426$ mT, $a(meta) = 0.16$ mT).

Acknowledgement

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