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### Preliminary communication

## CIDNP $^1\text{H}$ study of the photolysis of 7-sila- and 7-germa-norbornadienes

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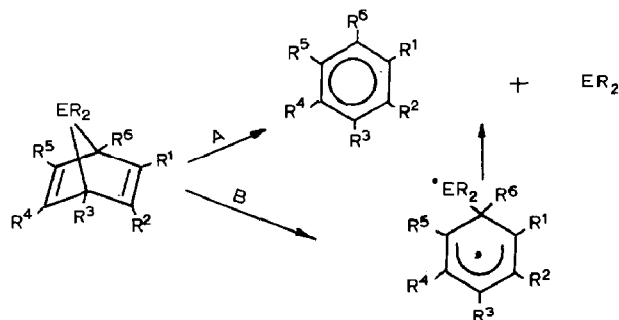
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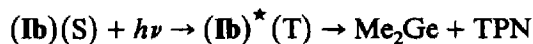
### Abstract

The photochemical decomposition of 7-sila- and 7-germa-norbornadienes (**Ia,b**) was studied by the CIDNP  $^1\text{H}$  technique. The reactions proceed by a two-step mechanism via the reversible formation of singlet biradicals, **II**. The triplet biradical (**III**), formed as a result of S–T conversion of (**II**)(S), irreversibly decomposes giving  $\text{Me}_2\text{E}$  (E = Si, Ge). The insertion of  $\text{Me}_2\text{E}$  into the C–Br bond of  $\text{PhCH}_2\text{Br}$  and the Sn–Cl bond of  $\text{Me}_3\text{SnCl}$  occurs via a radical mechanism, as deduced from the CIDNP effects observed in these reactions.

7-Sila- and 7-germa-norbornadienes (**I**) are convenient sources of the corresponding silylenes and germylenes under thermolysis or photolysis [1–6]. Two possible mechanisms for the decomposition of these compounds involving concerted (path A) or stepwise (path B) cleavage of endocyclic E–C( $sp^3$ ) bonds have been discussed [1,3,4,7].



Recently, the mechanism of photochemical decomposition of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germanorbornadiene (**Ib**) has been studied by flash photolysis and low-temperature matrix-isolation techniques [8,9]. The formation of a biradical precursor of dimethylgermylene has been proposed [9]:



In continuation of our investigations in this field we have studied the photolysis of 7-sila- and 7-germa-norbornadienes (**Ia,b**) by the CIDNP  $^1\text{H}$  technique. In the course of photolysis of **Ia,b** we observed CIDNP effects both for the starting compounds **Ia,b** (emission of  $\text{Me}_2\text{E}$  group signals of **Ia,b**) and for their decomposition product, 1,2,3,4-tetraphenylnaphthalene (TPN) (enhanced absorption of Ph-protons signals), see Fig. 1 and Table 1. The same pattern of **Ia,b** polarization was found when **Ia,b** were photolyzed in the presence of  $\text{Me}_2\text{E}$ -trapping agents (for example,  $\text{Me}_3\text{SnCl}$ ). These results show that the polarized **Ia,b** and TPN have a paramagnetic precursor, namely, a biradical II.

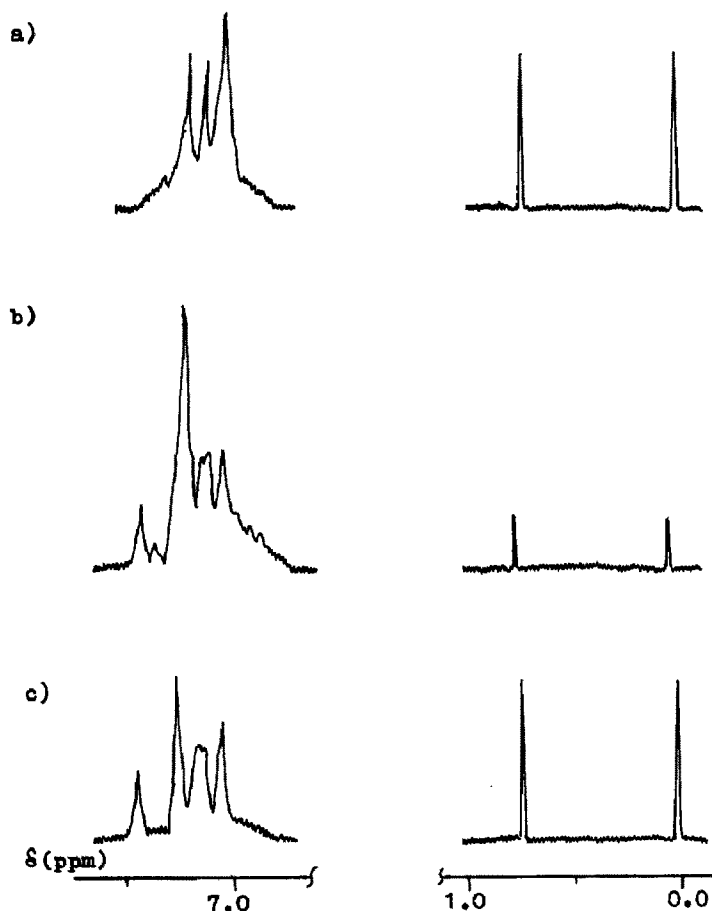


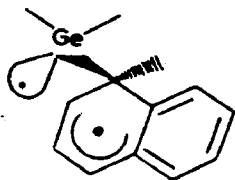
Fig. 1.  $^1\text{H}$  CIDNP during photolysis of **Ia** in  $\text{C}_6\text{D}_6$ : (a) before irradiation; (b) during UV irradiation (40 s after the start of irradiation); (c) after irradiation. CIDNP of **Ib** gave identical results (see Table 1)

Table 1

$^1\text{H}$  CIDNP during photolysis of **Ia** and **Ib** in the presence of  $\text{PhCH}_2\text{Br}$  and  $\text{Me}_3\text{SnCl}$  (A—enhanced absorption, E—emission)

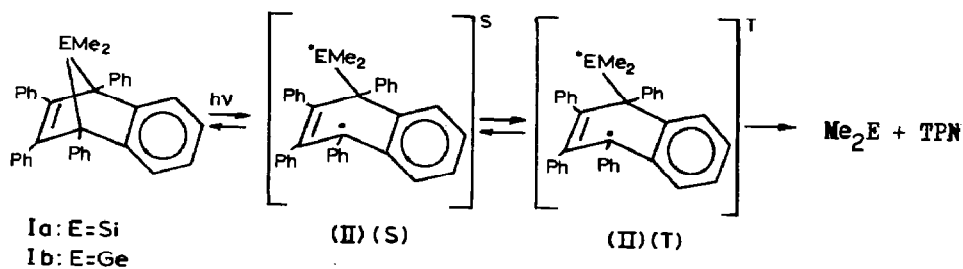
Assignment	$\delta$ (ppm)	CIDNP
$\text{GeMe}_2$ ( <b>Ia</b> )	0.22; 0.94	E; E
$\text{Me}_3\text{SnGeMe}_2\text{Cl}$	0.29	A
$\text{Me}_3\text{SnGeMe}_2\text{Cl}$	0.78	A
$\text{SiMe}_2$	0.05; 0.72	E; E
$\text{PhCH}_2\text{SiMe}_2\text{Br}$	0.39	E
$\text{PhCH}_2\text{SiMe}_2\text{Br}$	2.32	E
$\text{Me}_2\text{SiBr}_2$	0.80	A

Two mechanisms ( $\text{S-T}_0$  and  $\text{S-T}_-$ ) are proposed for CIDNP effects in biradicals [10,11]. CIDNP effects of opposite sign for the recombination (**Ia,b**) and decomposition (TPN) products of the biradical **II** testify in a favour of an  $\text{S-T}_0$  mechanism. This mechanism may be realized when CIDNP effects occur in the conformation characterized by a small exchange interaction between radical centers. A consideration of molecular models of biradical **II** shows that such a small exchange interaction occurs when the orientation of an odd-electron orbital of germanium and the  $\pi$ -system of the naphthalene rings is close to perpendicular:



Based on this assumption the CIDNP effects of **Ia,b** and TPN were analysed. The biradical was simulated by a radical pair with the magnetic resonance parameters of phenylmethylgermyl and cyclohexadienyl free radicals [12]

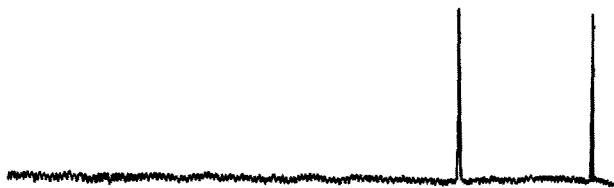
The use of Kaptein's rules [13] for the observed CIDNP effects shows that the singlet biradical (**II**(S)) is formed from the  $\text{S}_1$  state of **Ia,b**. The singlet biradical **II** recombines giving the polarized starting norbornadienes **Ia,b**. The triplet biradical **II**, formed as a result of  $\text{S-T}$  conversion, irreversibly decomposes with the formation of  $\text{Me}_2\text{E}$  ( $\text{E} = \text{Si, Ge}$ ) and polarized TPN.



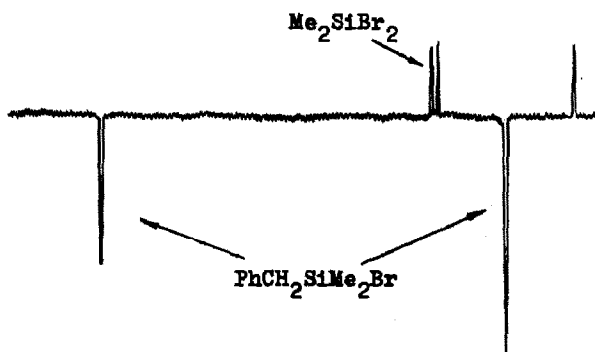
CIDNP effects were also observed in the course of insertions of  $\text{Me}_2\text{E}$ , photochemically generated from **Ia,b**, into the  $\text{C-Br}$  bond of  $\text{PhCH}_2\text{Br}$  and the  $\text{Sn-Cl}$

C4

a)



b)



c)

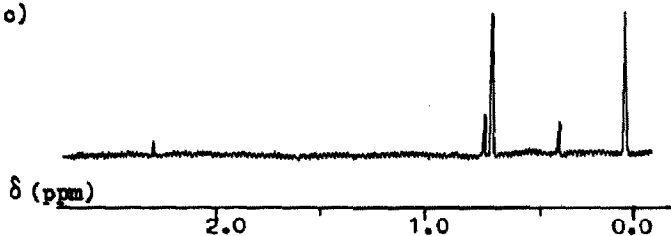
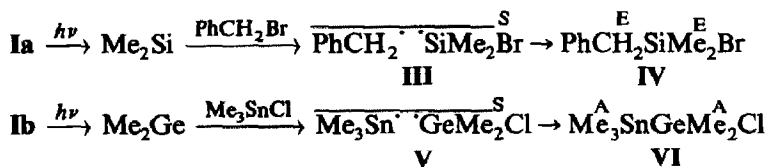


Fig. 2.  $^1\text{H}$  CIDNP during photolysis of **1a** in the presence of  $\text{PhCH}_2\text{Br}$  ( $20^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): (a) before irradiation; (b) during UV irradiation (40 s after the start of irradiation); (c) after irradiation.

bond of  $\text{Me}_3\text{SnCl}$  (see Figs. 2 and 3, and Table 1). The effects can be explained by the formation of radical pairs which are similar to those formed in the reactions of thermally generated  $\text{Me}_2\text{Ge}$  with halogen-containing compounds [5,14]. The radical pairs formed in the reactions of  $\text{Me}_2\text{E}$  with  $\text{PhCH}_2\text{Br}$  and  $\text{Me}_3\text{SnCl}$  were in a singlet state, as could be deduced from the CIDNP effects analysis based on Kaptein's rules [13].



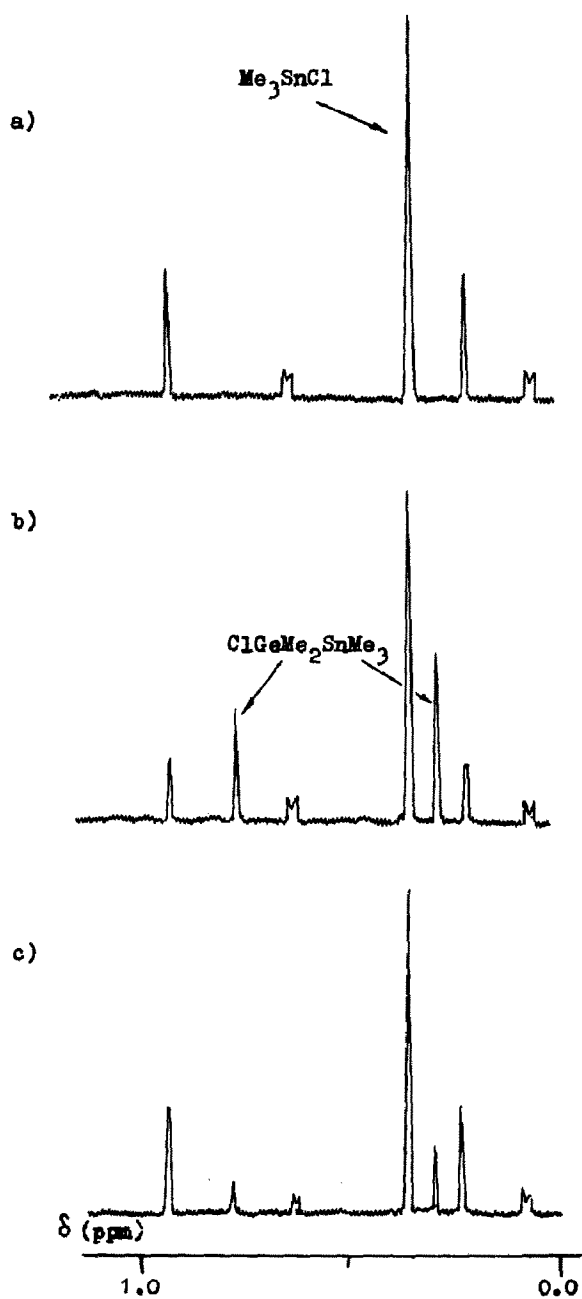


Fig. 3.  $^1\text{H}$  CIDNP during photolysis of **Ib** in the presence of  $\text{Me}_3\text{SnCl}$  ( $20^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ); (a) before irradiation; (b) during UV irradiation (40 s after the start of irradiation); (c) after irradiation.

The insertion product,  $\text{PhCH}_2\text{SiMe}_2\text{Br}$  (**IV**), is formed by recombination of the radical pair **III** (cage product). The formation of  $\text{Me}_2\text{SiBr}_2$  (a  $\cdot\text{SiMe}_2\text{Br}$  radicals escape product) and toluene was also observed in the reaction of **Ia** with  $\text{PhCH}_2\text{Br}$ . However, it must be pointed out that UV irradiation of a benzene solution of  $\text{PhCH}_2\text{Br}$  also produced noticeable quantities of toluene.

The CIDNP effects observed in the reaction of  $\text{Me}_2\text{Ge}$  with  $\text{Me}_3\text{SnCl}$  show that the insertion occurs via a cage abstraction–recombination process, but not via a one-step concerted mechanism as proposed earlier [4]. The absorption signal of  $\text{Me}_3\text{Sn}$ -group (instead of the proposed emission signal) could be explained by the exchange process between excess  $\text{Me}_3\text{SnCl}$  and the positive polarized diffusing  $\text{Me}_3\text{Sn}^{\cdot}$  radicals.

An analysis of the CIDNP signals of insertion products **IV** and **VI** indicates the singlet character of the reactive  $\text{Me}_2\text{E}$  ( $\text{E} = \text{Si, Ge}$ ) species. The singlet state of the reactive dimethylgermylene, thermally or photochemically generated from **Ib**, was also confirmed in refs. 8,9,14.

## Experimental

Norbornadienes **Ia,b** were photolyzed in quartz NMR tubes directly in the probe of a  $^1\text{H}$  NMR spectrometer (JEOL FX 90Q, pulsed, 90 MHz) with UV light of an Hg high pressure lamp (DRSH-500, 500 W, UFS-2 filter). The photolytical part of equipment was synchronized by a computer to the NMR spectrometer. NMR spectra were recorded after 40 s UV irradiation of the samples. The accumulation time of the FID is 4.5 s. The pulsed spectra were taken with 1 scan. The concentration of norbornadienes **Ia,b** in the samples was  $5 \times 10^{-3} \text{ M}$ .

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