

Preliminary communication

CIDNP ^1H study of the photolysis of 7-sila- and 7-germa-norbornadienes

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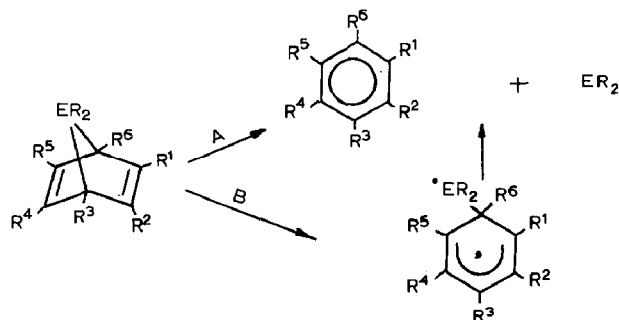
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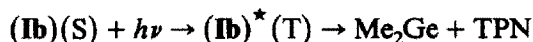
Abstract

The photochemical decomposition of 7-sila- and 7-germa-norbornadienes (**Ia,b**) was studied by the CIDNP ^1H technique. The reactions proceed by a two-step mechanism via the reversible formation of singlet biradicals, **II**. The triplet biradical (**II**), formed as a result of S–T conversion of (**II**)(S), irreversibly decomposes giving Me_2E (E = Si, Ge). The insertion of Me_2E into the C–Br bond of PhCH_2Br and the Sn–Cl bond of Me_3SnCl 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 ^1H technique. In the course of photolysis of **Ia,b** we observed CIDNP effects both for the starting compounds **Ia,b** (emission of Me_2E 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 Me_2E -trapping agents (for example, Me_3SnCl). These results show that the polarized **Ia,b** and TPN have a paramagnetic precursor, namely, a biradical II.

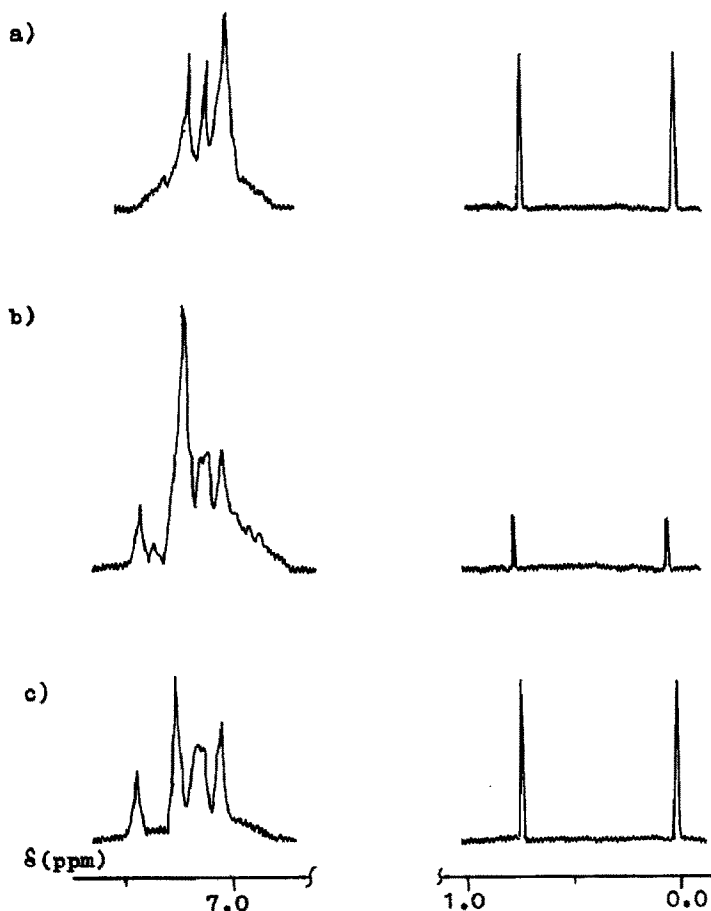


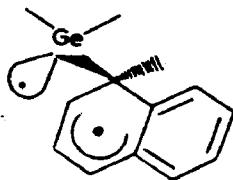
Fig. 1. ^1H CIDNP during photolysis of **Ia** in C_6D_6 : (a) before irradiation; (b) during UV irradiation (40 s after the start of irradiation); (c) after irradiation. CIDNP of **Ib** gave identical results (see Table 1)

Table 1

^1H CIDNP during photolysis of **Ia** and **Ib** in the presence of PhCH_2Br and Me_3SnCl (A—enhanced absorption, E—emission)

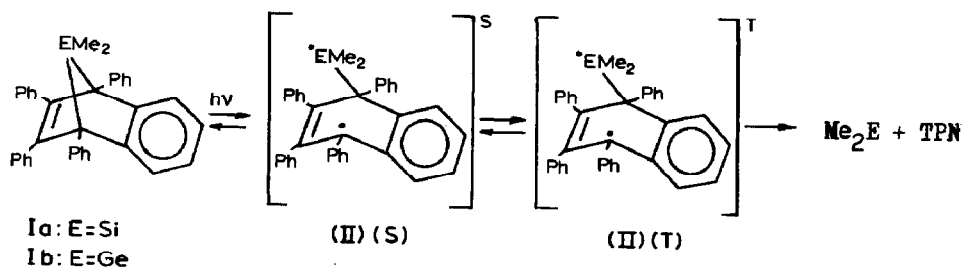
| Assignment | δ (ppm) | CIDNP |
|---------------------------------------|----------------|-------|
| GeMe_2 (Ia) | 0.22; 0.94 | E; E |
| $\text{Me}_3\text{SnGeMe}_2\text{Cl}$ | 0.29 | A |
| $\text{Me}_3\text{SnGeMe}_2\text{Cl}$ | 0.78 | A |
| SiMe_2 | 0.05; 0.72 | E; E |
| $\text{PhCH}_2\text{SiMe}_2\text{Br}$ | 0.39 | E |
| $\text{PhCH}_2\text{SiMe}_2\text{Br}$ | 2.32 | E |
| Me_2SiBr_2 | 0.80 | A |

Two mechanisms (S-T_0 and 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 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 π -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]

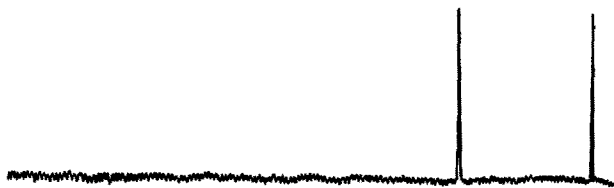
The use of Kaptein's rules [13] for the observed CIDNP effects shows that the singlet biradical (**II**(S)) is formed from the S_1 state of **Ia,b**. The singlet biradical **II** recombines giving the polarized starting norbornadienes **Ia,b**. The triplet biradical **II**, formed as a result of S-T conversion, irreversibly decomposes with the formation of Me_2E ($\text{E} = \text{Si, Ge}$) and polarized TPN.



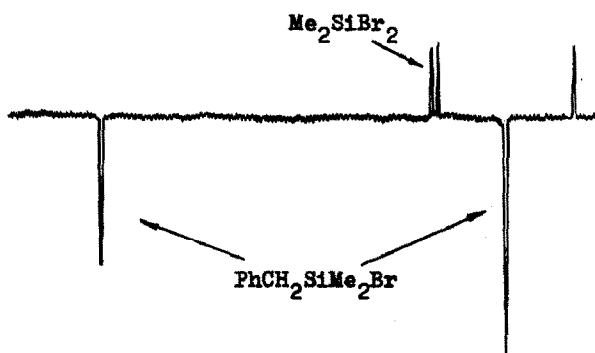
CIDNP effects were also observed in the course of insertions of Me_2E , photochemically generated from **Ia,b**, into the C-Br bond of PhCH_2Br and the Sn-Cl

C4

a)



b)



c)

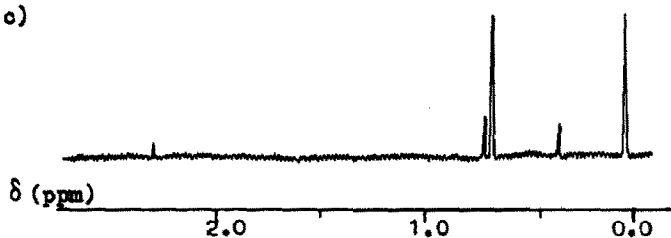
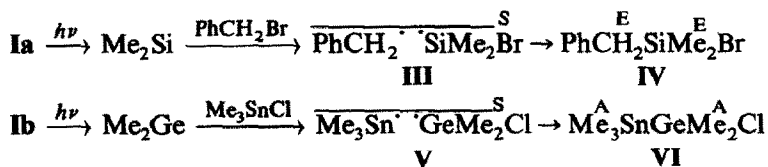


Fig. 2. ^1H CIDNP during photolysis of Ia in the presence of PhCH_2Br (20°C , C_6D_6): (a) before irradiation; (b) during UV irradiation (40 s after the start of irradiation); (c) after irradiation.

bond of Me_3SnCl (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 Me_2Ge with halogen-containing compounds [5,14]. The radical pairs formed in the reactions of Me_2E with PhCH_2Br and Me_3SnCl were in a singlet state, as could be deduced from the CIDNP effects analysis based on Kaptein's rules [13].



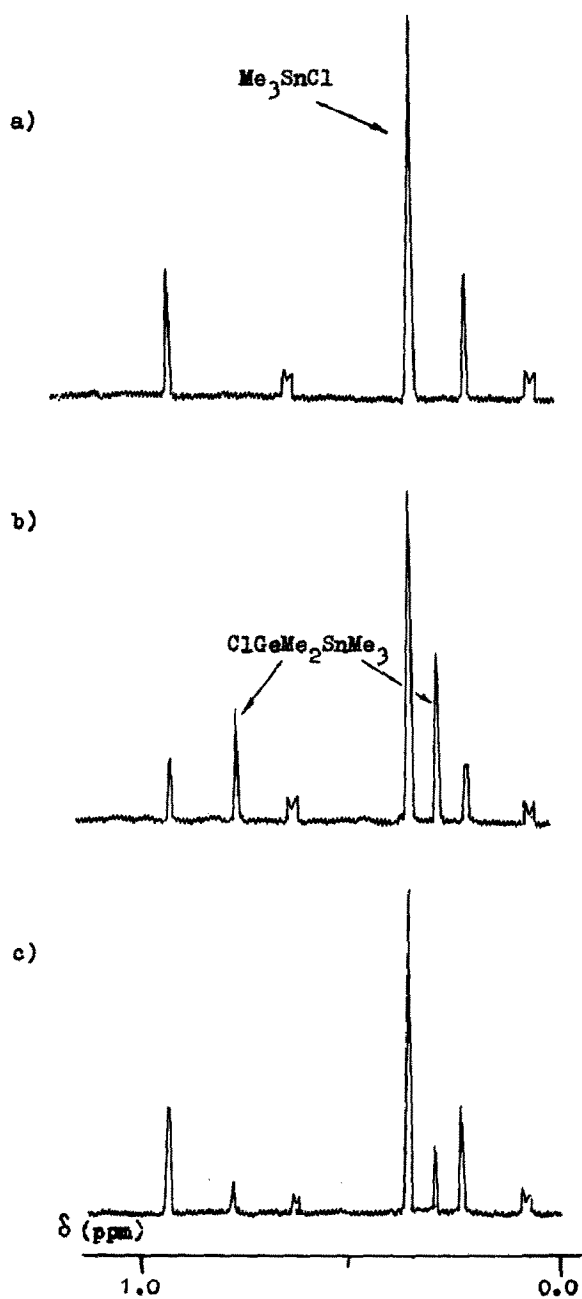


Fig. 3. ^1H CIDNP during photolysis of **Ib** in the presence of Me_3SnCl (20°C , C_6D_6); (a) before irradiation; (b) during UV irradiation (40 s after the start of irradiation); (c) after irradiation.

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 Me_2SiBr_2 (a SiMe_2Br radicals escape product) and toluene was also observed in the reaction of **Ia** with PhCH_2Br . However, it must be pointed out that UV irradiation of a benzene solution of PhCH_2Br also produced noticeable quantities of toluene.

The CIDNP effects observed in the reaction of Me_2Ge with Me_3SnCl 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 Me_3Sn -group (instead of the proposed emission signal) could be explained by the exchange process between excess Me_3SnCl 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 Me_2E ($\text{E} = \text{Si, Ge}$) 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 ^1H 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 $5 \times 10^{-3} \text{ M}$.

References

- 1 B. Mayer and W.P. Neumann, *Tetrahedron Lett.*, (1980) 4887.
- 2 J.A. Hawari and D. Griller, *Organometallics*, 3 (1984) 1123.
- 3 W.P. Neumann and M. Schriewer, *Tetrahedron Lett.*, 21 (1980) 3273.
- 4 M. Schriewer and W.P. Neumann, *J. Am. Chem. Soc.*, 105 (1983) 897.
- 5 J. Kocher, M. Lehnig and W.P. Neumann, *Organometallics*, 7 (1988) 1201.
- 6 O.M. Nefedov, M.P. Egorov, S.P. Kolesnikov, A.M. Galminas, Yu.T. Struchkov, M.Yu. Antipin and S.V. Sereda, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1986) 1693.
- 7 T.J. Barton, W.F. Goure, J.L. Witak and W.D. Wulff, *J. Organomet. Chem.*, 225 (1982) 87.
- 8 M.P. Egorov, A.S. Dvornikov, S.P. Kolesnikov, V.A. Kuzmin and O.M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 1200.
- 9 S.P. Kolesnikov, M.P. Egorov, A.S. Dvornikov, V.A. Kuzmin and O.M. Nefedov, *Metalloorganicheskaya Khim.*, 2 (1989) 799.
- 10 G.L. Closs and Ch.E. Doubleday, *J. Am. Chem. Soc.*, 95 (1973) 2735.
- 11 K.M. Salikov, Yu.N. Molin, R.Z. Sagdeev and A.L. Buchachenko, in: Yu.N. Molin (Ed.), *Spin Polarization and Magnetic Effects in Radical Reactions*. Akademiai Kiado, Budapest, 1984, 419 p.
- 12 H. Fisher and K.-H. Hellwege (Eds.), *Landolt-Bornstein New Series. Numerical Data and Functional Relationship in Science and Technology; Magnet Properties of Free Radicals, Group II, Vol. 9, Part A,B,C*, Springer-Verlag, Berlin, 1979.
- 13 R. Kaptein, *Chem. Commun.*, (1971) 732.
- 14 J. Kocher and M. Lehnig, *Organometallics*, 3 (1984) 937.