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Mendeleev Commun., 1991, 1(4), 143–145

Mendeleev
Communications

# $^1$H CIDNP Study of the Addition Reaction of $Me_2E$ (E = Si,Ge) to a Carbon≡Carbon Triple Bond

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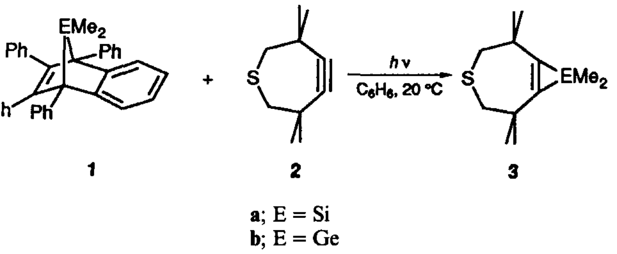
Addition of $Me_2E$ (E = Si,Ge) to the triple bond of 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne proceeds in a nonconcerted way *via* a 1,3-biradical intermediate; the first experimental evidence of the participation of an excited triplet $Me_2E$ species in a chemical reaction has been obtained.

The addition of $R_2E$ (E = Si, Ge) to carbon≡carbon triple bonds is one of the most important reactions of silylenes and germylenes. This results, in some cases, in the formation of stable strained three-membered heterocycles: the sila(germa)-cyclopropenes.[1,2] However, there is no experimental data on the mechanism of these reactions.

We describe here the mechanism of the addition reactions of dimethylgermylene and dimethylsilylene, generated photochemically from the corresponding derivatives of 7-sila(germa)norbornadienes **1a,b**, with the triple bond of 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne **2** giving the sila(germa)-cyclopropenes **3a,b** in quantitative yield (Scheme 1).[2]

The mechanism has been studied by the $^1$H CIDNP technique (chemically induced dynamic nuclear polarisation). It has been found that the reaction proceeds in a nonconcerted way *via* a 1,3-biradical intermediate. Analysis of the CIDNP indicates that the $Me_2E$ species are in an excited triplet state when they react with **2**. This is the first experimental evidence of the participation of a triplet $Me_2E$ (E = Si,Ge) species in a chemical reaction.

Norbornadienes **1a,b** were photolysed directly in quartz NMR tubes in the probe of $^1$H NMR spectrometer (JEOL FX 90Q, pulsed, 90 MHz) with UV radiation from a Hg high pressure lamp (DRSH-500, 500 W, UFS-2 filter). The photolytic part of the equipment was synchronized with the computer of the NMR spectrometer. The NMR spectra were recorded after 40 s UV irradiation of the samples. The accumulation time for FID is 4.5 s. The pulsed spectra were taken with 1 scan. The concentration of norbornadienes **1a,b**, $PPh_3$ and thiacycloheptyne **2** in the samples was $5 \times 10^{-3}$ mol dm$^{-3}$.



**1** **2** **3**

**a**; E = Si
**b**; E = Ge

**Scheme 1**

During the photolysis of **1b** and **2** (20 °C, $C_6D_6$, $[\mathbf{1b}] = [\mathbf{2}] = 5 \times 10^{-3}$ mol dm$^{-3}$) we observed CIDNP effects both for the starting compounds (emission of $Me_2Ge$ group signals for **1b** and emission of a Me group signal for **2**) and for the reaction product **3b** (enhanced absorption of the $Me_2Ge$- and Me-group signals), see Fig. 1 and Table 1. The same CIDNP effects, (considerably weaker, however, possibly as a result of the slower rate of photolysis of **1a**) were observed during the photolysis of **1a** in the presence of **2**.

We have described previously how polarization of **1a,b** occurs during the course of their photodecomposition, proceeding *via* a biradical species.[3] The $^1$H CIDNP effects observed for the products **3a,b** show that the polarized sila- and germa-cyclopropenes **3a,b** have a paramagnetic precursor, namely biradical **4**.

In the case of 'short' biradicals, *i.e.*, 1,3-biradicals, CIDNP effects with opposite signs for a starting compound and for a product indicate the operation of the $T_0$-S mechanism.[4] In 1,3-biradical **4** the exchange integral $|J|$ is close to zero because of the orthogonality of the odd-electron orbitals, see Fig. 2. The realization of the $T_0$-S mechanism for the CIDNP effects in **4**

**Table 1** $^1$H CIDNP effects observed during photochemical reactions of **1a** and **1b** with thiacycloheptyne **2**

| Assignment | δ | CIDNP[a] |
|---|---|---|
| $GeMe_2$ (**1b**) | 0.22; 0.94 | E; E |
| $SiMe_2$ (**1a**) | 0.05; 0.72 | E; E |
| Me– (**2**) | 1.15 | E |
| $-CH_2-$ (**2**) | 2.69 | – |
| $GeMe_2$ (**3b**) | 0.50 | A |
| Me– (**3b**) | 1.22 | A |
| $-CH_2-$ (**3b**) | 2.69 | – |
| $SiMe_2$ (**3a**) | 0.21 | A |
| Me– (**3a**) | 1.22 | A |
| $-CH_2-$ (**3a**) | 2.65 | – |

[a] A: enhanced absorption; E: emission.

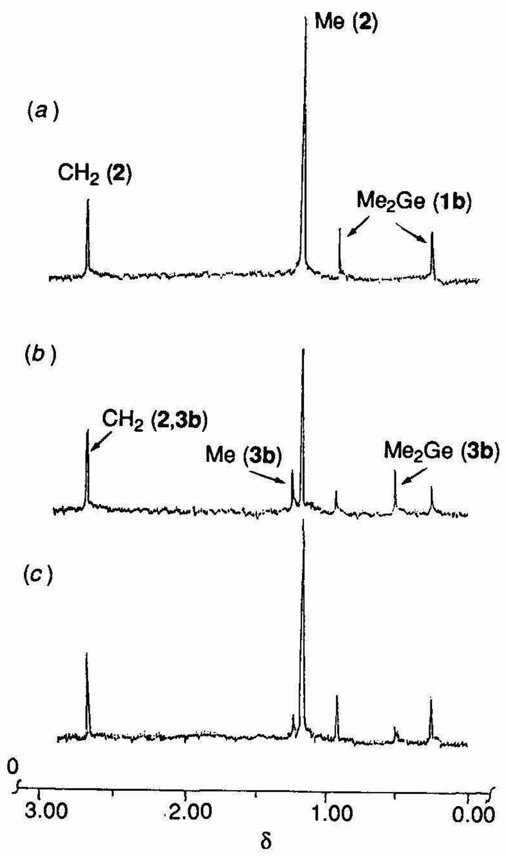
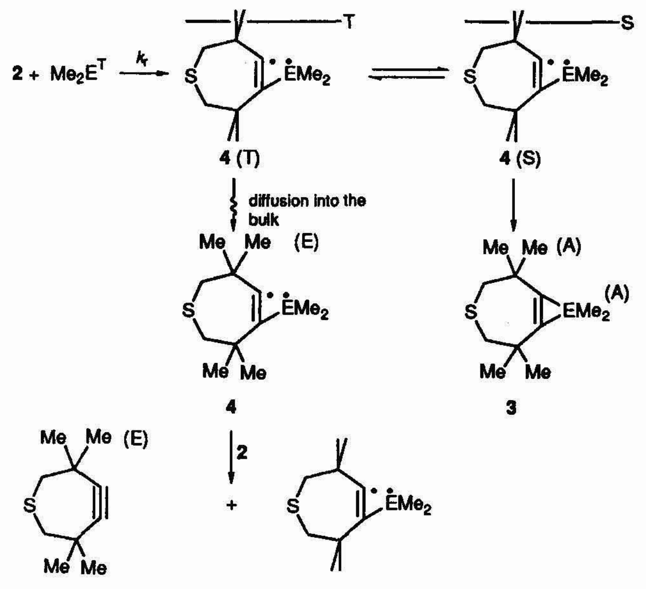


**Fig. 1** $^1$H CIDNP effects observed during photochemical reactions of **1b** with thiacycloheptyne **2** (20 °C, $C_6D_6$): (*a*) before irradiation; (*b*) during UV irradiation (40 s after the beginning of irradiation); (*c*) after irradiation)

means that $2|J| << g\mu_BH_0$, where $g$ is gyromagnetic ratio, $\mu_B$ is the Bohr magneton and $H$ is magnetic field.

The triplet state of the initial biradical **4** may be deduced from an analysis of the CIDNP signals according to Kaptein's rules[5] [$a_{Me_2E}(H) > 0$, $a_{Me} < 0$, $g$ values of biradical **4** are not known; however, the $g$ values of all known germanium-centred radicals are usually greater than those of carbon-centred radicals,[6] *e.g.*, $g(Me_3Ge\cdot) = 2.0104$,[7] $g(H_2C{=}CH\cdot) = 2.0022$[8]] within the framework of the $T_0$-S mechanism. The polarized heterocyclopropenes **3** form as cage recombination products. The polarized thiacycloheptyne **2** forms as an escape product. The polarization of **2** develops as a result of an exchange of $Me_2E$ species between the negatively polarized biradical **4** diffusing into the bulk and thiacycloheptyne **2** (Scheme 2).

In order to confirm Scheme 2, the photolysis of **1b** has been carried out in the presence of triphenylphosphine, a singlet dimethylgermylene scavenger (it forms the $Me_2Ge{\cdot}PPh_3$ complex with dimethylgermylene[9]). We observed analogous CIDNP effects for the starting compound **1b** (emission of $Me_2Ge$ group signals) and for the reaction product **3b** (enhanced absorption of $Me_2Ge$- and Me-group signals) upon UV irradiation of a 1:1:1 mixture of **1b**, **2** and $PPh_3$. However, the CIDNP effects for the starting compound thiacycloheptyne **2** disappeared during the reaction. Therefore, as expected, the addition of $PPh_3$ does not change the CIDNP cage effect arising in the reaction of $Me_2Ge(T)$ with **2** (CIDNP effects for **3b**) but affects the CIDNP effects from the diffusing biradicals **4**. There may be no exchange reaction between diffusing **4** and **2** in the presence of $PPh_3$, because of the competing reaction of **4** with $PPh_3$.



E = Si, Ge

**Scheme 2**

The formation of biradical **4** in a triplet state indicates that the $Me_2E$ (E = Si, Ge) species reacting with **2** are in a triplet excited state. This conclusion is quite important. Indeed, triplet $R_2E$ species are a subject of particular experimental and theoretical interest.[10–12] However, all reactions of silylenes and germylenes studied up till now were reactions of singlet $R_2E$ species.

It is known that singlet carbenes usually react with substrates in concerted ways while stepwise reactions proceeding *via* radical species are typical for triplet carbenes.[13,14] From this point of view the observation of CIDNP effects during the addition of $Me_2E$ to the triple bond of **2** shows the triplet character of the reacting $Me_2E$ species.

We shall consider the mechanism of **1b** photolysis in order to explain the participation of triplet $Me_2E$ (E = Si,Ge) in the reaction. It has been shown by flash photolysis[15] and $^1$H CIDNP[3] techniques that photodecomposition of **1b** occurs from a triplet excited state. Therefore, one could expect the formation of an excited triplet $Me_2Ge$ in this case. However, the dimethylgermylene detected during the photolysis of **1b** reacts with the trapping agents, including thiacycloheptyne **2** in its ground singlet state.[3,15,16] This may be a result of both the lower reactivity of $Me_2Ge(T)$ compared with that of $Me_2Ge(S)$ and the fast intersystem crossing $Me_2Ge(T) \xrightarrow{k_{ISC}} Me_2Ge(S)$ facilitated by the heavy germanium atom.

In the case of a highly reactive trapping agent R the reaction of $Me_2Ge(T)$ with R could compete with intersystem crossing, *i.e.* $k_r^T[R] > k_{ISC}$, where $k_r$ is the rate constant for the reaction of **2** with $Me_2Ge(T)$, and $k_{ISC}$ is the rate constant for intersystem crossing. The most effective scavenger of $Me_2Ge(S)$, following from the kinetic data, is the strained thiacycloheptyne **2** ($k_r = 5.0 \times 10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$).[15] Our results show that the reactivity of **2** towards the $Me_2Ge(T)$ addition reaction is also high and that the reaction of **2** with $Me_2Ge(T)$ competes with intersystem crossing.

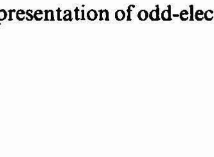


**Fig. 2** Schematic representation of odd-electron orbitals in biradical **4**

*Received in USSR, 27th May 1991*
*Received in UK, 12th June 1991; Com. 1/02829D*

*Mendeleev Commun.*, 1991, 1(4), 143–145

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