Spin chemistry of organometallic compounds
2. Interaction of *N*-bromohexamethyldisilazane with allyltriorganolsilanes

Marc B. Taraban [a,*], Alexander I. Kruppa [a], Nikolai E. Polyakov [a], Mikhail G. Voronkov [b], Vladimir I. Rakhlin [b], Stanislav V. Grigor'ev [b], Olga S. Volkova [a], Rudolph G. Mirskov [b], Tatyana V. Leshina [a]

[a] *Laboratory of Magnetic Phenomena, Institute of Chemical Kinetics and Combustion, Street 3, 630090 Novosibirsk 90, Russia*
[b] *Irkutsk Institute of Chemistry, 664033 Irkutsk 33, Russia*

Abstract

Two instances have been considered demonstrating the influence of organoelement substituent on the reactivity of radicals generated from $R_3MCH_2CH=CH_2$ (M = Si or Sn) in photoinduced interaction with $(Me_3Si)_2NBr$. CIDNP studies has allowed to identify two different reaction mechanisms for M = Si or M = Sn which end up in two different sets of reaction products. © 2002 Published by Elsevier Science B.V.

1. Introduction

Recently, we have reported the unusual photoinduced interaction of *N*-bromohexamethyldisilazane ($Me_3Si)_2NBr$ with allyltriethylstananne $Et_3SnCH_2CH=CH_2$ resulting in the nearly quantitative yield of allene [1].

To understand the effect of the element atom properties as well as the influence of the attached substituents we have studied similar reactions of *N*-bromohexamethyldisilazane with allyltriorganosilanes $R_3MCH_2CH=CH_2$ (M = Si; R = Me, Et, OMe, OEt, Cl). It has been found that, in these cases, the direction of the process is completely changed, and the reaction results in a complex mixture of products, some of them most likely originated in the secondary processes. In all cases, main reaction products include hexamethyldisila-

zane ($Me_3Si)_2NH$, bromotriorganosilane R_3SiBr, allylhexamethyldisilazane $(Me_3Si)_2NCH_2CH=CH_2$, allyl bromide $CH_2=CHCH_2Br$, and corresponding addition products.
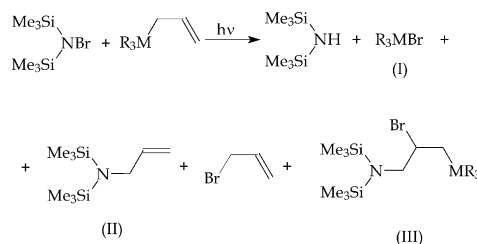
The addition products (**III**) were isolated, though with low yields, and characterized. Organoelement compounds with the acceptor substituent of β-carbon atom with respect to element are unstable [2,3], therefore, during the reaction, III is partially decomposed into bromotriorganometallanes R_3MBr (**I**) and allylhexamethyldisilazane $(Me_3Si)_2NCH_2CH=CH_2$ (**II**). This explains the presence of these species in the resulting reaction mixture. The presence of the allyl bromide $CH_2=CHCH_2Br$ could be due to the β-cleavage of the unstable dibromide $R_3MCH_2CHBrCH_2Br$ (**IV**)—an

intermediate product formed through the bromine addition to the initial allylic substrate. This particular pathway of the intermediate formation of dibromide is in agreement with [4], where the possibility of the active role of both $(Me_3Si)_2N^{\bullet}$ and $^{\bullet}Br$ radicals in the reactions of *N*-bromohexamethyldisilazane has been explicitly demonstrated.

Thus, on the basis of the isolated products, the photoinduced interaction of $(Me_3Si)_2NBr$ with allyltriorganosilanes could be represented by the following scheme of the radical chain reaction (Scheme 1). The proposed mechanism is consistent with the reference data [5,6] on the possibility of the addition of $(Me_3Si)_2N^{\bullet}$ radical to double bond.

However, the hydrogen atom abstraction from the olefin molecule is also a very characteristic reaction pathway for the $(Me_3Si)_2N^{\bullet}$ radical [4]. This process also takes place in the reaction under study where hexamethyldisilazane $(Me_3Si)_2NH$ is one of the main reaction products. One might propose the following mechanism of $(Me_3Si)_2NH$ formation, again, through the radical chain reaction scheme (Scheme 2).

Unfortunately, we have failed to isolate the products of the transformations of the abstraction product, the allylic radical $R_3M\dot{C}HCH=CH_2$, possibly, due to their further bromination. Alternatively, the $(Me_3Si)_2N^{\bullet}$ radical could enter the addition reaction to these allylic species followed by the photocleavage of the resulting adduct.
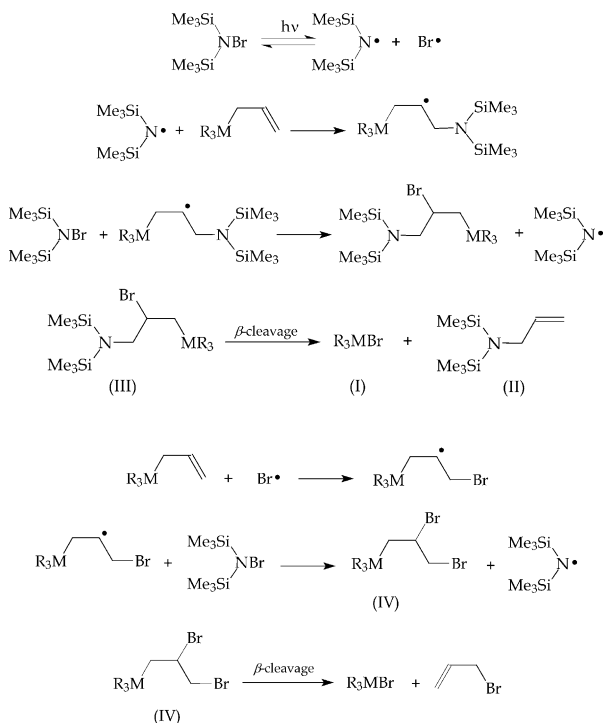
Scheme 1. Radical chain reaction of $(Me_3Si)_2NBr$ and $R_3MCH_2CH=CH_2$ (M = Si).
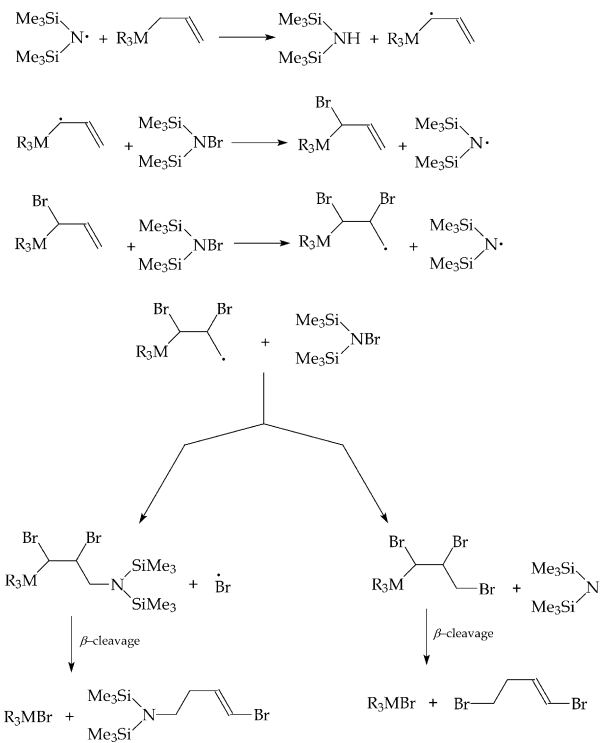
Scheme 2. Formation of $(Me_3Si)_2NH$ through radical chain process.

Depending on the nature of the substituents attached to the element, the reaction mixture could contain some other secondary reaction products. For instance, along with R_3SiBr, the formation of Me_3SiBr has been observed which is an evidence of the exchange reaction between bromotriorganosilane and hexamethyldisilazane.

R = Me, Et, MeO, EtO
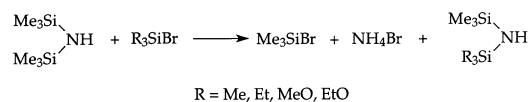
In the case of allyltrichlorosilane $Cl_3SiCH_2CH=CH_2$, the reaction mixture also contained chlorotrimethylsilane Me_3SiCl also formed through the exchange reaction of bromotrichlorosilane with $(Me_3Si)_2NH$:
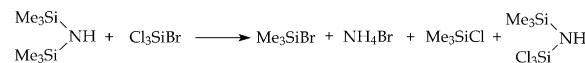
Photoinduced interaction of allyltriorganosilanes was also studied by means of ^1H CIDNP. The photolysis of allyltrimethylsilane $Me_3SiCH_2CH=CH_2$ with $(Me_3Si)_2NBr$ has allowed to detect CIDNP effects of the protons of addition product $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$, allylhexamethyldisilazane $(Me_3Si)_2NCH_2CH=CH_2$, and allyl bromide $CH_2=CH-CH_2Br$ (Fig. 1). Polarization was also observed in the reactions of allyltrialkoxysilanes, however, the enhancement coefficients were substantially lower. The investigations of the photolytic processes directly in the probe of NMR spectrometer have shown that the substitution
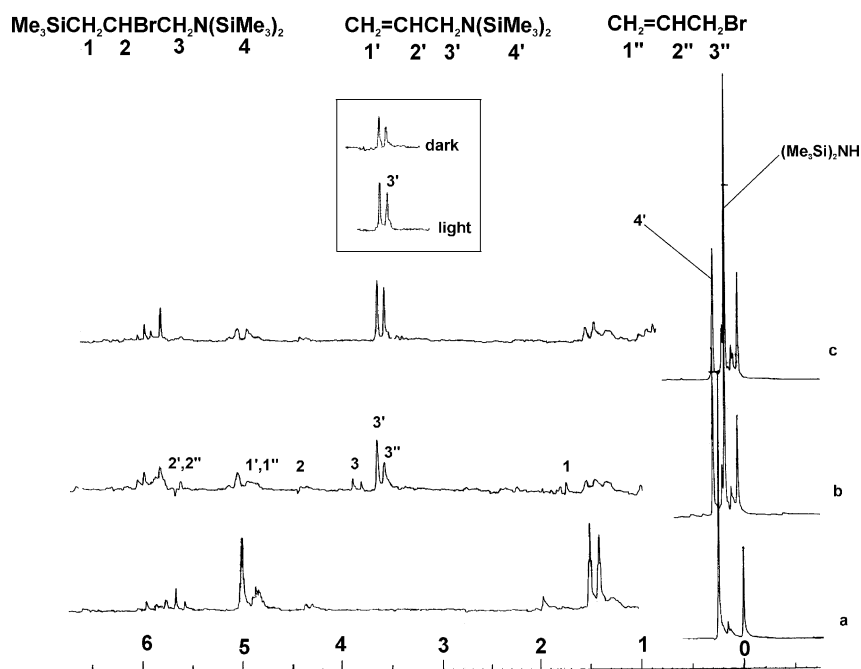
Fig. 1. ^{1}H CIDNP effects observed during the photoinduced interaction of $Me_3SiCH_2CH=CH_2$ with two-fold excess of $(Me_3Si)_2NBr$ in C_6D_6; (a) initial spectrum; (b) under UV irradiation; (c) spectrum after irradiation. Numbers correspond to the proton groups of the reaction products. The inset shows the region of $>NCH_2$-protons for the case of equal concentrations of the reagents.

of the alkyl groups at silicon atom with more acceptor ones such as methoxy or ethoxy, will result in significant slow down of the reaction rate, though the observation of CIDNP effect still points to the existence of the radical stages. In the case of allyltrichlorosilane $Cl_3SiCH_2CH=CH_2$ containing the most active acceptor substituents—three chlorine atoms—the reaction rate further drops downs, and polarization effects completely disappear.

It is necessary to mention that the observation of CIDNP effects testify to the fact that the products are formed through the radical pairs (RP). From the analogy of the earlier studied photoinduced reactions of allyl derivatives of Si, Ge, and Sn with $BrCCl_3$ [7,8], and the interactions of $Et_3SnCH_2CH=CH_2$ with $(Me_3Si)_2NBr$ [1], the following considerations were taken into account when analyzing the observed CIDNP effects. RP responsible for CIDNP generation in similar photoinitiated reactions are formed on a random encounter of the partner radicals in the bulk (so-called *F*-pairs, with $\mu > 0$, see rules for analysis in the Section 2). In the above mentioned papers these pairs were comprised of radical-adduct $R_3MCH_2\dot{C}HCH_2CCl_3$ and $\dot{}CCl_3$ radical. The RPs involving bromine atom are undoubtedly present in the bulk, however, due to high spin-orbital coupling of $\dot{}Br$ they are incapable to generate CIDNP effects. In the reaction with $(Me_3Si)_2NBr$, one cannot exclude the formation of the RP of $(Me_3Si)_2N\dot{}$ and $R_3\dot{M}CHCH=CH_2$ radicals, since the abstraction of hydrogen atom from the olefin by $(Me_3Si)_2N\dot{}$ radical is postulated to be one of the basic functions of this

radical [4] (see also Scheme 1). However, taking into account the composition of the products, the analysis of CIDNP effects of the addition product and the resulting allylhexamethyldisilazane $CH_2=CHCH_2N(SiMe_3)_2$ (see Scheme 1) will be performed assuming that these polarization effects were formed in the RP of $\dot{}CH_2CHBrCH_2SiR_3$ and $(Me_3Si)_2N\dot{}$ free radicals.

Thus, to clarify the mechanism of the process under study, CIDNP effects observed during the photoinduced interaction of $Me_3SiCH_2CH=CH_2$ with $(Me_3Si)_2NBr$ were analyzed according to the common rules (see, Section 2 for the details) [9]. As seen from Fig. 1, the addition product $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$ demonstrates pronounced polarization of $-CH_2N<$ protons ($\delta = 3.85$ ppm, A for absorption) and much weaker effects of $-CHBr-$ ($\delta = 4.48$ ppm, E for emission) and $Si-CH_2-$ ($\delta = 1.80$ ppm, A) protons. The above distribution of the net CIDNP intensities points to the formation of the polarization effects in the free diffusion uncorrelated radical pair (*F*-pair) of $\dot{}CH_2CHBrCH_2SiR_3$ and $(Me_3Si)_2N\dot{}$ free radicals (RP-1). Indeed, in this case, highest HFI constant and, correspondingly, highest polarization effects should be characteristic for α-CH_2-protons of the radical. The addition product $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$ should result from the cage recombination of the above RP-1.

Following magnetic resonance parameters of the partner radicals of the RP-1 were used for the analysis of the observed CIDNP effects. The conclusions were made assuming that *g*-factor of $(Me_3Si)_2N\dot{}$ radical is
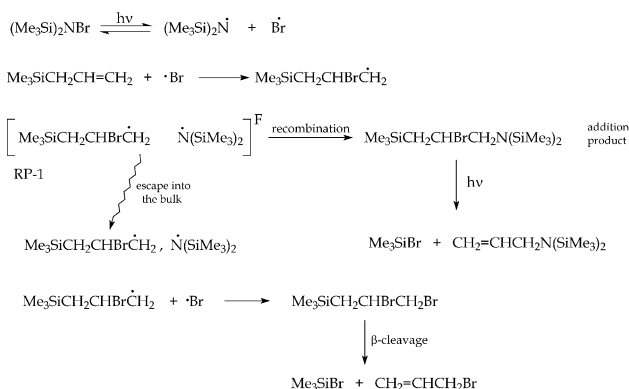
greater than that of its carbon-centered partner in the radical pair, and the HFI constants of Me-protons in $(Me_3Si)_2N^\bullet$ radical are positive. Bromosubstituted $^\bullet CH_2CHBrCH_2SiR_3$ radical has the following HFI constants: $A(\alpha\text{-}CH_2) < 0$, $A(CHBr) > 0$, $A(CH_2Si-) < 0$ [10].

Absorption (A) of the $-CH_2N<$ protons of the addition product $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$

$$(\frac{\mu \;\cdot\; \varepsilon \;\cdot\; \Delta g \;\cdot\; A}{+ \;\cdot\; - \;\cdot\; + \;\cdot\; -} = +(A),$$

see, Section 2 for details) suggests the possibility of the polarized $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$ to result from cage recombination of RP-1. Whereas allyl bromide $CH_2=CHCH_2Br$ should be polarized as an escape product of this pair, i.e. it will demonstrate emission (E) of $-CH_2Br$ protons. Indeed, CIDNP spectra show this emission at $\delta = 3.43$ ppm (Fig. 1). The presence of the polarization effects and their sign points to the escape of the polarized bromosubstituted $^\bullet CH_2CHBrCH_2SiR_3$ radical into the bulk. In accordance with above assumption, possible attack of one bromine atom in the bulk will lead to the β-cleavage of the resulting dibromide (Scheme 3)

Unfortunately, it was not possible to analyze the polarization of allyl bromide protons at the double bond—these signals overlap with the lines from the initial $Me_3SiCH_2CH=CH_2$ ($\delta = 4.87$ ppm ($CH_2=$); 5.67 ppm ($=CH$); see also Fig. 1). The signals from the corresponding protons of allylhexamethyldisilazane $CH_2=CHCH_2N(SiMe_3)_2$ are also located in this region ($\delta = 5.09$ ppm ($CH_2=$); 5.69 ppm ($=CH$)). In accordance with the above considerations one should expect that $CH_2=CHCH_2N(SiMe_3)_2$ resulting from the β-cleavage of the addition product, if polarized at all, will demonstrate in-cage CIDNP effects. This will be the case if the rate of β-cleavage is greater than the spin-lattice relaxation of the protons of addition product ($T_1 \sim 6$–7 s [7]). Thus, $-CH_2-N<$ protons ($\delta = 3.63$ ppm) should demonstrate positive polarization (absorp-

tion). In practice, however, this effect is not necessarily observed in all experiments, and is dependent on the concentration of the initial $Me_3SiCH_2CH=CH_2$. This effect might result from one more RP formed in the act of photodecomposition of the addition product $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$. The fact that in contrast to preparative photolysis, under more intensive irradiation of the reaction mixture we have failed to observe the accumulation of the addition product may mean that this compound undergoes the photodecomposition. Thus, by analogy with the mechanism of β-cleavage of similarly structured tin-containing compounds [1,7] one might expect the formation of the singlet RP (RP-2) of the radicals resulting from the photodecomposition of the addition product (Scheme 4).

Following ^1H CIDNP effects could be generated in the RP-2: $-CH_2Si$

$$\frac{\mu \;\cdot\; \varepsilon \;\cdot\; \Delta g \;\cdot\; A}{- \;\cdot\; + \;\cdot\; - \;\cdot\; -} = -(E), \text{ emission;}$$

$-CHBr-$

$$\frac{\mu \;\cdot\; \varepsilon \;\cdot\; \Delta g \;\cdot\; A}{- \;\cdot\; + \;\cdot\; - \;\cdot\; +} = +(A), \text{ absorption;}$$

and $-CH_2N<$

$$\frac{\mu \;\cdot\; \varepsilon \;\cdot\; \Delta g \;\cdot\; A}{- \;\cdot\; + \;\cdot\; - \;\cdot\; -} = -(E), \text{ weak emission.}$$
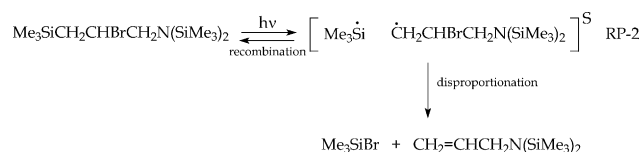
One might also expect to observe emission

$$(\frac{\mu \;\cdot\; \varepsilon \;\cdot\; \Delta g \;\cdot\; A}{- \;\cdot\; + \;\cdot\; + \;\cdot\; +} = -(E))$$

of Me_3Si-protons. Since these protons do not demonstrate the polarization, while those of $(Me_3Si)_2N$-group of $(Me_3Si)_2NCH_2CH=CH_2$ show the pronounced absorption ($\delta = 0.30$ ppm), one might conclude that the contribution of RP-2 to the resulting CIDNP effects of this group is negligible, and the observed absorption is generated in RP-1

$$(\frac{\mu \;\cdot\; \varepsilon \;\cdot\; \Delta g \;\cdot\; A}{+ \;\cdot\; + \;\cdot\; + \;\cdot\; +} = +(A))$$

(cf. Schemes 3 and 4).

Thus, in principle CIDNP effects of $(Me_3Si)_2NCH_2CH=CH_2$ represent the superposition of the contributions from the polarization's formed in RP-

Scheme 3. Radical pair mechanism of the photoinduced interaction of $Me_3SiCH_2CH=CH_2$ in the presence of $(Me_3Si)_2NBr$.

Scheme 4. Tentative pathway of the decomposition of the addition product $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$.

1 and RP-2, and the latter contribution appears to be concentration dependent.

The additional information of the detailed mechanism of the process under study could be also obtained from the analysis of ^{1}H CIDNP effects of the Me$_3$Si-protons of the initial (Me$_3$Si)$_2$NBr (emission, $\delta = 0.22$–0.26 ppm, depending on the concentration) and those of the reaction product hexamethyldisilazane, (Me$_3$Si)$_2$NH (absorption, $\delta = 0.13$–0.15 ppm). The negative polarization of (Me$_3$Si)$_2$NBr (E) is most likely transferred to the molecule of the initial (Me$_3$Si)$_2$NBr through chemical exchange between (Me$_3$Si)$_2$N$^\bullet$ radical escaped from the recombination of RP-1 (Scheme 3) and the initial N-bromohexamethyldisilazane, as it has been already shown for the photoinduced interaction of (Me$_3$Si)$_2$NBr with allyltriethylstannane Et$_3$SnCH$_2$CH=CH$_2$ [1].

$$(\overset{*}{Me_3Si})_2N\cdot \; + \; (Me_3Si)_2NBr \longrightarrow (\overset{*}{Me_3Si})_2NBr \; + \; (Me_3Si)_2N\cdot$$
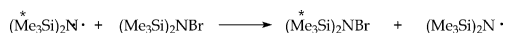
* denotes the polarized protons

As for the ^{1}H CIDNP effect of (Me$_3$Si)$_2$NH, the observed positive polarization of Me$_3$Si-protons testifies that hexamethyldisilazane is a cage recombination product resulting from hydrogen atom abstraction from Me$_3$SiĊHCH=CH$_2$ radical by the polarized (Me$_3$Si)$_2$N$^\bullet$ radical. Recent studies of the photoinduced interaction of Et$_3$SnCH$_2$CH=CH$_2$ with (Me$_3$Si)$_2$NBr [1] have shown that (Me$_3$Si)$_2$NH was one of the main reaction products. The formation of (Me$_3$Si)$_2$NH in [1] was accompanied by generation of allene CH$_2$=C=CH$_2$ and R$_3$MBr. In the present case, taking into account the absence of allene as well as its precursor among the reaction products and also the absence of corresponding signals in CIDNP spectra, it is suggested that the polarization of (Me$_3$Si)$_2$NH is generated from other sources (formed in another RP). One of the possible candidates could be the above mentioned radical pair of (Me$_3$Si)$_2$N$^\bullet$ and Me$_3$SiĊHCH=CH$_2$ free radicals. Unfortunately, at this stage it is impossible to identify other products of this RP, since the expected retention of the double bond in these products makes it impossible to identify their CIDNP effects due to the signal overlap with the analogous groups of (Me$_3$Si)$_2$NCH$_2$CH=CH$_2$, CH$_2$=CH–CH$_2$Br, and the initial Me$_3$SiCH$_2$CH=CH$_2$.

Thus, summarizing the above analysis of CIDNP effects and judging from the set of reaction products of the photoinduced interaction of N-bromohexamethyldisilazane (Me$_3$Si)$_2$NBr with allyltriorganosilanes R$_3$SiCH$_2$CH=CH$_2$ (R = Me, Cl, OMe) the following conclusion could be made. In contrast to the earlier studied reaction between (Me$_3$Si)$_2$NBr and Et$_3$SnCH$_2$CH=CH$_2$ [1], the reaction under study results in a much broader set of the reaction products, therefore, one could not exclude the possibility of their formation through radical chain mechanism presented in Scheme 1.

However, the following regularity have engaged the attention when analyzing the mechanisms of formation of the reaction products of the photoinduced interaction of N-bromohexamethyldisilazane (Me$_3$Si)$_2$NBr with allylic tin [1] and silicon derivatives. The definitive stage of the formation of main reaction products is the interactions in the uncorrelated radical pair (F-pair) of R$_3$MCH$_2$CHBrĊH$_2$ and (Me$_3$Si)$_2$N$^\bullet$ radicals (Scheme 5).

When M = Sn, the disproportionation of the radical pair becomes the main reaction pathway, while for M = Si, only the recombination occurs. Undoubtedly, this difference is caused by the influence of the element atom, and this is in agreement with the earlier obtained evidences that the effect of silicon- and germanium-containing substituents on the radical addition reactions is distinctly different from that of tin-containing groups [7,8].

Thus, there are two instances of the influence of organoelement substituent on the radical reactivity. Despite the apparent triviality, these results are, in fact, unusual—the nature of the influence of organoelement function on the direction of the process, e.g. hydrogen atom abstraction by another radical or the recombination, undoubtedly deserves further detailed investigations. At this stage, one might only suggest that organotin substituents having more pronounced donor properties as compared with organosilicon and organogermanium ones, facilitate the homolytic C–H cleavage.

2. Experimental

GLC analysis was carried out using 'Tsvet 500' (heat conductivity detector, He, glass column 3 m × 4 mm, 10% PMS-1000 on a Chromaton N-AW-HMDS, 0.20–0.25 mm grain). NMR spectra were taken for 10–15% solutions in CDCl$_3$ ('Izotop') by means of JEOL JNM FX 90Q high-resolution NMR spectrometer (90 MHz for protons) and BRUKER DPX-400 (400 MHz for protons) using Me$_4$Si, HMDS as internal standards. ^{1}H CIDNP spectra were detected by means JEOL JNM FX90Q equipped special in-house device for the irradiation of the samples directly in the probe of the spectro-
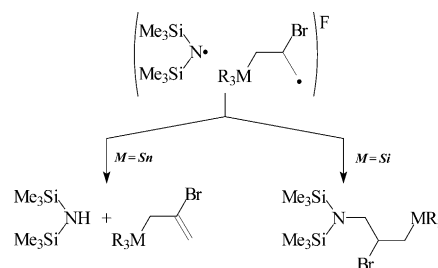
Scheme 5. Alternative pathways of the transformations of the RP-precursor of the main reaction products.

meter. Irradiation was carried out in standard Pyrex NMR tubes using the full light of a DRSH-1000 high-pressure mercury lamp (1 kW). A thermal filter used to prevent the heating of the sample.

The analysis of CIDNP effects was carried out using the existing rules [9]. The sign of net CIDNP effect (Γ) observed in high magnetic field is defined by the product of multiplication of the following parameters:

$$\Gamma = \mu \cdot \varepsilon \cdot \Delta g \cdot A$$

where μ is the multiplicity of the RP-precursor ('+' for triplet and uncorrelated pair, and '−' for singlet precursor), ε is '+' for 'in-cage' and '−' for' escape recombination products, Δg is the sign of difference in g-factors of the radical with polarized nucleus and radical partner in the RP, A is the sign of hyperfine interaction constant of nucleus under study in the radical. The sign of Γ reflects the phase of the NMR signal of nucleus under study: '+' for enhanced absorption (A) and '−' for the emission (E). For example, if one consider certain group of, say, protons in the product resulting from the recombination (ε is '+') of the uncorrelated RP (μ is '+'), and if this group has belonged to the radical with the g-factor smaller than that of the partner radical of the RP (Δg is '−'), and if the sign of hyperfine interaction for this particular group in the radical is negative (A is '−'), then the multiplication gives

$$\frac{\mu \cdot \varepsilon \cdot \Delta g \cdot A}{+ \cdot + \cdot - \cdot -} = +(A),$$

and one should observe the enhanced absorption of the NMR signal of this group.

2.1. Reaction of Me₃SiCH₂CH=CH₂ with (Me₃Si)₂NBr

2.1. Reaction of $Me_3SiCH_2CH{=}CH_2$ with $(Me_3Si)_2NBr$

The mixture of 11 g (0.096 M) of allyltrimethylsilane and 23 g (0.096 M) of $(Me_3Si)_2NBr$ was degassed according to freeze-pump-thaw techinque and then subjected to UV irradiation (UV lamp DRT-400) during 10 h in a sealed glass tube. Following product were isolated by fractional distillation: Me_3SiBr (2.7 g), $CH_2{=}CHCH_2Br$ (1.3 g), $(Me_3Si)_3NH$ (1.5 g), $CH_2{=}CHCH_2N(SiMe_3)_2$ (4.5 g), and the addition product $Me_3SiCH_2CHBrCH_2N(SiMe_3)_2$ (3.7 g), yield 11%, b.p. 61 °C/2 mm; $n_D^{21} = 1.4127$, δ (^{1}H) in CDCl$_3$: 0.08 (s, 18 H, Me$_3$Si^1), 0.45 (s, 9H, Me$_3$Si^2), 1.75 (m, 2H, –CH$_2$Si), 3.63 (m, 2H, >NCH$_2$–), 4.53 (m, 1H, –CHBr–).

2.2. Reaction of $Et_3SiCH_2CH{=}CH_2$ with $(Me_3Si)_2NBr$

The reaction was carried out similar to the above mentioned interaction of $Me_3SiCH_2CH{=}CH_2$ with $(Me_3Si)_2NBr$ (paragraph 1) for the mixture of 17 g (0.11 M) of $Et_3SiCH_2CH{=}CH_2$ and 26.5 g (0.11 M) of

$(Me_3Si)_2NBr$. The fraction (6 g) containing Me_3SiBr, $CH_2{=}CHCH_2Br$, $(Me_3Si)_2NH$ (identified by means of GLC, in the ratio 2:1:6) was collected as well as $CH_2{=}CHCH_2N(SiMe_3)_2$ (3.5 g), Et_3SiBr (3.6 g), and the addition product $Et_3SiCH_2CHBrCH_2N(SiMe_3)_2$ (6.6 g), yield 15%, b.p. 85 °C/2 mm, $n_D^{23} = 1.4522$; δ (^{1}H) in CDCl$_3$: 0.07 (s, 18H, Me$_3$Si); 0.57 (m, 6H, –CH$_2$Si); 0.99 (m, 9H, CH$_3$–); 0.96 (m, 2H, –CH$_2$Si–); 2.99 (m, 2H, NCH$_2$); 3.66 (m, 1H, CHBr).

2.3. Reaction of $(MeO)_3SiCH_2CH{=}CH_2$ with $(Me_3Si)_2NBr$

The mixture of 14 g (0.086 M) of $(MeO)_3SiCH_2CH{=}CH_2$ and 21 g (0.086 M) of $(Me_3Si)_2NBr$ was subjected to UV irradiation during 4 h. The irradiation was stopped when the reaction mixture became turbid. The following products were isolated by fractional distillation: the mixture of Me_3SiBr and $(Me_3Si)_2NH$ (5.4 g) in the ratio 1:5, the initial $(MeO)_3SiCH_2CH{=}CH_2$ (3.8 g), and the addition product $(MeO)_3SiCH_2CHBrCH_2N(SiMe_3)_2$ (3.5 g), yield 10%, b.p. 81 °C/3 mm, $n_D^{19} = 1.4567$, δ (^{1}H) in CDCl$_3$: 0.07 (s, 18H, MeSi); 3.88 (s, 9H, (MeO)$_3$Si); 1.87 (m, 2H, CH$_2$Si); 3.13 (m, 2H, –NCH$_2$–); 4.18 (m, 1H, CHBr). $CH_2{=}CHCH_2N(SiMe_3)_2$ (2.7 g) has also been isolated.

2.4. Reaction of $(EtO)_3SiCH_2CH{=}CH_2$ with $(Me_3Si)_2NBr$

The mixture of 6.6 g (0.032 M) of $(EtO)_3SiCH_2CH{=}CH_2$ and 7.7 g (0.032 M) $(Me_3Si)_2NBr$ was subjected to UV irradiation. The irradiation was stopped when the reaction mixture became turbid. The following products were isolated by fractional distillation: the mixture of Me_3SiBr, $(EtO)_3SiBr$, and $(Me_3Si)_2NH$ (4 g) in the ratio 4:1:7, the initial $(EtO)_3SiCH_2CH{=}CH_2$ (2.6 g), and the addition product $(EtO)_3SiCH_2CHBrCH_2N(SiMe_3)_2$ (1.7 g), yield 11%, b.p. 105 °C/4 mm, $n_D^{20} = 1.4582$, δ (^{1}H) in CDCl$_3$: 0.08 (s, 18H, Me$_3$Si); 1.34 (m, 9H, CH$_3$–); 3.79 (m, 6H, –CH$_2$OSi); 1.84 (m, 2H, –CH$_2$Si); 3.11 (m, 2H, >NCH$_2$); 4.2 (m, 1H, –CHBr).

2.5. Reaction of $Cl_3SiCH_2CH{=}CH_2$ with $(Me_3Si)_2NBr$

The mixture of 7.6 g (0.043 M) of $Cl_3SiCH_2CH{=}CH_2$ and 10.4 g (0.043 M) of $(Me_3Si)_2NBr$ was subjected to UV irradiation during 14 h. The following product were isolated by fractional distillation: the mixture of Me_3SiCl, Me_3SiBr, Cl_3SiBr, and $(Me_3Si)_2NH$ (3.6 g) in the ratio 6:2:4:1, $CH_2{=}CHCH_2N(SiMe_3)_2$ (1.5 g), and the addition product $Cl_3SiCH_2CHBrCH_2N(SiMe_3)_2$ (2.4 g), yield 13.4%, B.p. 123 °C/3 mm, δ (^{1}H) in CDCl$_3$: 0.42 (s, 18H, Me$_3$Si); 2.26 (m, 2H, –CH$_2$Si); 3.87 (m, 2H, >NCH$_2$); 3.87 (m, 1H, CHBr). δ (^{29}Si) in CDCl$_3$: 31.10 (s,

Cl$_3$Si), 7.29 (s, (Me$_3$Si)$_2$N). The mixture also contained 4 g of unreacted Cl$_3$SiCH$_2$CH=CH$_2$.

Acknowledgements

References

[1] M.B. Taraban, A.I. Kruppa, V.I. Rakhlin, S.V. Grigor'ev, O.S. Volkova, R.G. Mirskov, T.V. Leshina, J. Organomet. Chem. 636 (2001) 12.

[2] R.W. Bott, C. Eaborn, B.M. Ruston, J .Organomet. Chem. 3 (1965) 445.

[3] M.A. Cook, C. Eaborn, D.R.M. Walton, J. Organomet. Chem. 24 (1970) 301.

[4] B.P. Roberts, C. Wilson, J. Chem. Soc. Chem. Commun. (1978) 752.

[5] M.D. Cook, B.P. Roberts, K. Singh, J. Chem. Soc. Perkin Trans. II (1983) 635.

[6] J.C. Brand, B.P. Roberts, J.N. Winter, J. Chem. Soc. Perkin Trans. II (1983) 261.

[7] T.V. Leshina, R.Z. Sagdeev, N.E. Polyakov, V.I. Valyaev, M.B. Taraban, V.I. Rakhlin, R.G. Mirskov, S.Kh. Khangazheev, M.G. Voronkov, J. Organomet. Chem. 259 (1983) 295.

[8] T.V. Leshina, V.I. Valyaev, M.B. Taraban, V.I. Maryasova, V.I. Rakhlin, S.Kh. Khangazheev, R.G. Mirskov, M.G. Voronkov, J. Organomet. Chem. 299 (1986) 271.

[9] R. Kaptein, Chem. Commun. (1971) 732.

[10] According to reference data from Landolt-Börnstein New Series. Numerical Data and Functional Relationship in Science and Technology, H. Fischer, K.-H. Hellwege (Eds.); Springer-Verlag, Berlin, 1979, Parts B–D, g-factor of R$_2$N$^\bullet$ radicals amounts to 2.0040, and the presence of the attached Me$_3$Si-groups will slightly increase this value. g-factor of $^\bullet$CH$_2$CHBrCH$_2$SiR$_3$ is ≤2.003, analogous species could be found in the above reference book.