



Spin chemistry of organometallic compounds 5. Interaction of N-bromohexamethyl disilazane with substituted silyl hydrides

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ABSTRACT

Reaction of N-bromohexamethyl disilazane $(\text{Me}_3\text{Si})_2\text{NBr}$ with substituted triorganyl silanes $\text{R}^1\text{R}^2\text{R}^3\text{SiH}$ results in asymmetric disilazanes $\text{Me}_3\text{SiNHSiR}^1\text{R}^2\text{R}^3$ and bromination product, bromotrimethyl silane Me_3SiBr . The reaction has demonstrated an unusual dependence on specific solvation. In benzene, bromination occurs immediately after mixing of the reagents, while in cyclohexane, the reaction products are formed only under UV-irradiation. Application of photoinduced CIDNP method has shown that the mechanism of bromination of triorganyl silanes is comprised of a series of consecutive radical stages involving N-centered disilazanyl $(\text{Me}_3\text{Si})_2\text{N}^\cdot$ and Si-centered silyl $\text{R}^1\text{R}^2\text{R}^3\text{Si}^\cdot$ radicals.

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1. Introduction

N-bromohexamethyl disilazane $(\text{Me}_3\text{Si})_2\text{NBr}$ (**1**) is well-known as a very convenient and smooth brominating agent widely used in the organic and organoelement syntheses. However, apart from outdated and disperse data on the interactions of **1** with organic derivatives of Group 14 elements – e.g., the reaction of **1** with N-sodiumhexamethyl disilazane [**1**], trimethylstannyl lithium [**2**], bivalent germanium species, and bis-(trimethylsilylamides) of tin and lead [**3**] – modern literature lacks the detailed study of its reactivity and reaction mechanisms when attacking the element-hydrogen bond. In our previous papers, we have successfully applied ¹H CIDNP (chemically induced dynamic nuclear polarization) method to explore in details the structure of paramagnetic intermediates of the photoinduced bromination of allyltrialkyl silanes, germanes and stannanes $\text{CH}_2=\text{CHCH}_2\text{MR}_3$ (M=Si, R=Me, Et, OMe, OEt, Cl; M=Ge, Sn, R=Et) by N-bromohexamethyl disilazane **1** [**4,5**].

To extend the synthetic potential of **1** and to get better insight into the mechanistic details, we have studied the reaction of **1** and a series of silyl hydrides $\text{R}^1\text{R}^2\text{R}^3\text{SiH}$ (**2**) with Si–H bond. On the

analogy of the reaction between triphenyl silane and bromine or N-bromosuccinimide [**6,7**], one might expect that bromotriorganyl silanes would also be the major ultimate bromination products of the reaction between **1** and **2**.

In the present paper, ¹H CIDNP method was used to study the detailed mechanism of the reaction of **1** with various silyl hydrides – dimethylphenyl silane PhMe_2SiH (**2a**), methyldiphenyl silane Ph_2MeSiH (**2b**), triphenyl silane Ph_3SiH (**2c**), triethoxysilane $(\text{EtO})_3\text{SiH}$ (**2d**), 1,1,3,3-tetramethyl disiloxane $\text{Me}_2\text{HSiOHSiHMe}_2$ (**2e**), 1,1,3,3-tetramethyl disilazane $\text{Me}_2\text{HSiN(H)SiHMe}_2$, and (**2f**), trichlorosilane Cl_3SiH (**2g**). We have also observed and discussed the effect of media polarity on the reactivity of **1** in the reaction with Si–H bond.

2. Results and discussion

Reactions of equimolar quantities of **1** and **2a–g** result in high yields of asymmetric 1,1,1-trimethyl-3,3,3-triorganyl disilazane **3a–g** and bromotrimethyl silane **4** (see Table 1 and Scheme 1). All reactions are strongly exothermic.

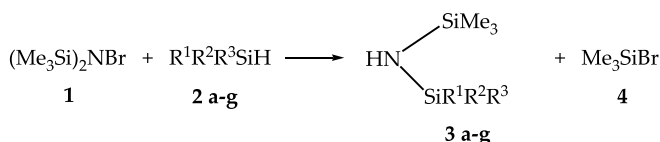
Two solvents were used as a reaction media when studying the interaction of **1** with **2a–g**. We have found that solvent properties drastically affect the reactivity of **1** as a bromination agent. In cyclohexane, **1** reacts with **2a–g** only under UV-irradiation, while

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Table 1

Major products and yields of the reaction of N-bromohexamethyl disilazane with silyl hydrides.

Silyl hydride	Major reaction products	Yield (%)
PhMe ₂ SiH (2a)	PhMe ₂ SiN(H)SiMe ₃ (3a)	46.6
Ph ₂ MeSiH (2b)	Ph ₂ MeSiN(H)SiMe ₃ (3b)	83.0
Ph ₃ SiH (2c)	Ph ₃ SiN(H)SiMe ₃ (3c)	69.2
(EtO) ₃ SiH (2d)	(EtO) ₃ SiN(H)SiMe ₃ (3d)	51.7
Me ₂ HSiO ₂ SiHMe ₂ (2e)	Me ₂ HSiO ₂ SiMe ₂ N(H)SiMe ₃ (3e)	43.9
Me ₂ HSiN(H)SiHMe ₂ (2f)	Me ₂ HSiN(H)SiMe ₂ N(H)SiMe ₃ (3f)	51.9
Cl ₃ SiH (2g)	Cl ₃ SiN(H)SiMe ₃ (3g)	59.6



- 2a** R¹ = Ph, R²=R³= Me;
2b R¹= R²= Ph, R³= Me;
2c R¹= R²=R³= Ph;
2d R¹= R²=R³= EtO-;
2e R¹= R²= Me, R³= Me₂HSiO-;
2f R¹=R²= Me, R³= Me₂HSiN(H)-;
2g R¹= R²=R³= Cl

Scheme 1. Reaction of N-bromohexamethyl silazane (**1**) with silyl hydrides.

in benzene, the reaction products are formed immediately after mixing of the reagents.

2.1. Photoinduced reaction of N-bromohexamethyl disilazane with silyl hydrides

In our previous papers [4,5], we have used ¹H CIDNP method to demonstrate that photoinduced bromination of different substrates by **1** is initialized by homolytic dissociation of N–Br bond of **1**, i.e., the photoinduced reaction follows a radical pathway driven by (Me₃Si)₂N• and •Br free radicals. ¹H CIDNP method was also used in the present paper to unravel the structure of paramagnetic intermediates and to suggest the radical stages of the photolysis of organosubstituted silyl hydrides **2a–g** in the presence of N-bromohexamethyl disilazane **1**. To this end, the mixture of **1** and one of **2a–g** in cyclohexane was irradiated directly in the probe of the NMR-spectrometer.

As an example of characteristic ¹H CIDNP effects, let us consider Fig. 1 which shows NMR spectra of the reaction mixture of **1** and **2c** before, under UV-irradiation, and after the photolysis. As seen from Fig. 1, we observe CIDNP effects of the protons of initial disilazane **1** (δ 0.25 ppm, emission, E) and the reaction product (δ 0.1 ppm, absorption, A). Similar CIDNP effects have been detected in the photoinduced reactions of **1** with other silyl hydrides **2a–g**. Therefore, the conclusion was made that photoinduced bromination of organosubstituted silyl hydrides **2a–g** by **1** follow similar radical reaction pathway.

Observation of CIDNP effects testify to the fact that polarized reaction products are generated through the elementary step involving the formation of the radical pair (RP). As we have shown in our previous papers [4,5], the first step of the photodecomposition of **1** is the cleavage of N–Br bond of (Me₃Si)₂NBr resulting in (Me₃Si)₂N• and •Br radicals. However, high spin-orbit coupling constant of Br radical would seriously affect spin-correlation in the initial RP, effectively mixing S- and T-states of initial radical pair composed of (Me₃Si)₂N• and •Br radicals and precluding the formation of CIDNP effects. Therefore, similar to the inference made in our previous papers [4,5], we have concluded that observed CIDNP

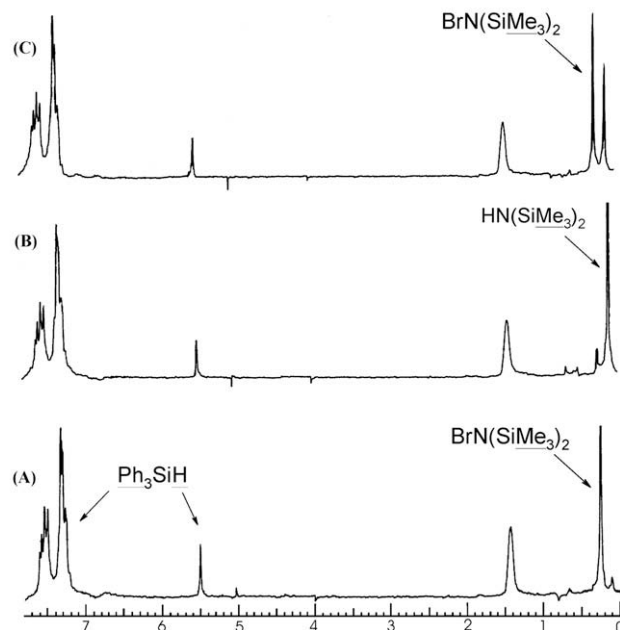
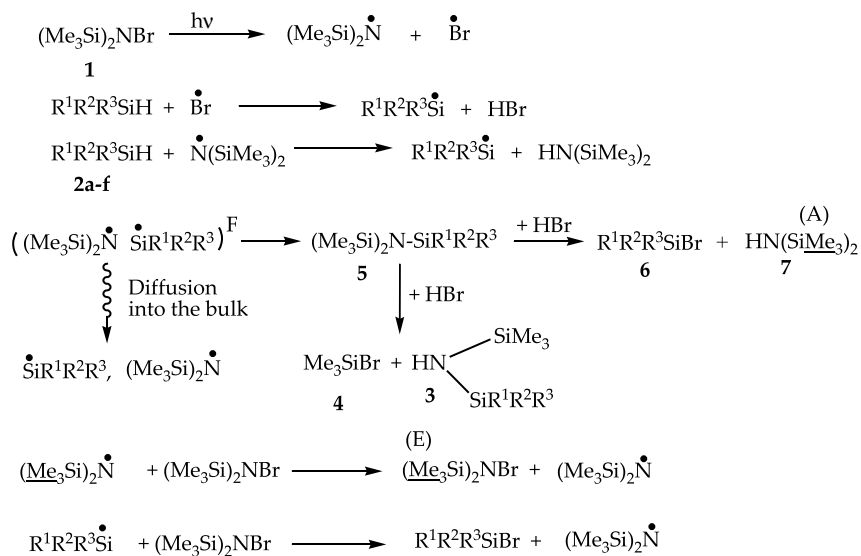


Fig. 1. 90 MHz ¹H CIDNP spectra in photoinduced reaction of Ph₃SiH (**2c**) and (Me₃Si)₂NBr (**1**) in cyclo-C₆D₁₂: (A) initial spectrum; (B) spectrum under UV-irradiation; (C) spectrum after photolysis.

effects are formed in the RPs originated from the random encounters of the radicals in the bulk (so-called diffusion or F-pairs). In the reaction under study, the silazanyl radical (Me₃Si)₂N• and silyl radical R¹R²R³Si• are the most sound candidates to form F-pair which would be a precursor of principal reaction products and a source of the observed polarization effects. Silyl radical R¹R²R³Si• could result from the interaction of silyl hydride **2a–g** with •Br radical and/or silazanyl radical (Me₃Si)₂N• with the synchronous formation of olefin by HBr and (Me₃Si)₂NH. Indeed, hydrogen abstraction from olefin by (Me₃Si)₂N• is postulated as one of its basic reactions [8,9]. All radical and nonradical reaction steps are summarized in Scheme 2.

To verify the proposed scheme we have analyzed the observed CIDNP effects based on the following magnetic resonance parameters of the involved free radicals. The sign of hyperfine interaction (HFI) constants of methyl protons in (Me₃Si)₂N• radical is positive; g-factor of the (Me₃Si)₂N• is suggested to be greater than that of its silicon-centered partner, R¹R²R³Si•, in radical F-pair (Scheme 2), since g-factors of R₂N• radicals typically amount to 2.0040 and in the case of two adjacent Me₃Si-groups this value would be even greater, whereas g-factors of R¹R²R³Si• radicals are about 2.0030 [10].

The radicals forming F-pair might recombine or escape into the bulk. In that case, the products of in-cage recombination and those of the reactions in the bulk would demonstrate CIDNP effects of the opposite signs. According to Scheme 2, the in-cage recombination of F-pair results in trisilazane **5**. At the same time, it is known that the addition of HBr promotes the dissociation of Si–N bonds [11]. Therefore, the alternative cleavage of two different Si–N bonds in trisilazane **5**, (Me₃Si)₂N–SiR¹R²R³, in the presence of HBr (Scheme 2) would result in silylbromides **4** and **6** along with the asymmetric (**3**) and the symmetric (**7**) disilazanes. Under the experimental conditions used for CIDNP observations, major decomposition product of trisilazane **5** is hexamethyldisilazane **7**. This was also confirmed by GS/MS analysis of the reaction mixture after irradiation. Note that CIDNP effects were observed only for Me₃Si-protons of hexamethyldisilazane **7** (absorption (A), Fig. 1 and Scheme 2), while one would otherwise expect to see the polarizations of trisi-



‡ Polarized Me-groups are underlined; (A) is enhanced absorption, (E) is emission.

Scheme 2. Elementary steps of photoinduced bromination of silyl hydrides by N-bromohexamethyl disilazane (**1**) (polarized Me-groups are underlined; (A) is enhanced absorption, (E) is emission).

lazane **5** which is primary recombination product of the precursor F-pair in Scheme 2. This is quite possible if the rate of Si–N bond cleavage in trisilazane **5** in the presence of HBr is competing with the rate of spin-lattice relaxation of Me₃Si-protons in **5**, and the product resulting from such cleavage – hexamethyldisilazane **7** – will demonstrate in-cage CIDNP effect. For F-pair the multiplicity factor μ is positive ($\mu = (+)$); the in-cage recombination factor ε is positive ($\varepsilon = (+)$); and as it has been suggested above, the relationship between the g -factors of the partner radicals obeys the inequality $g((\text{Me}_3\text{Si})_2\dot{\text{N}}) > g(\text{R}^1\text{R}^2\text{R}^3\dot{\text{Si}})$, so the difference of radical g -factors, Δg , is also positive ($\Delta g = (+)$); and the sign of HFI constant A of Me₃Si-protons in $(\text{Me}_3\text{Si})_2\dot{\text{N}}$ radical is also positive ($A = (+)$), therefore, the product of these factors $\mu \times \varepsilon \times \Delta g \times A = (+) \times (+) \times (+) \times (+)$ is positive and corresponds to the enhanced absorption (A) (see Section 3 for more details). Thus, experimentally observed positive polarization of Me₃Si-protons of **7** (δ 0.1 ppm, Fig. 1) is in agreement with the proposed Scheme 2.

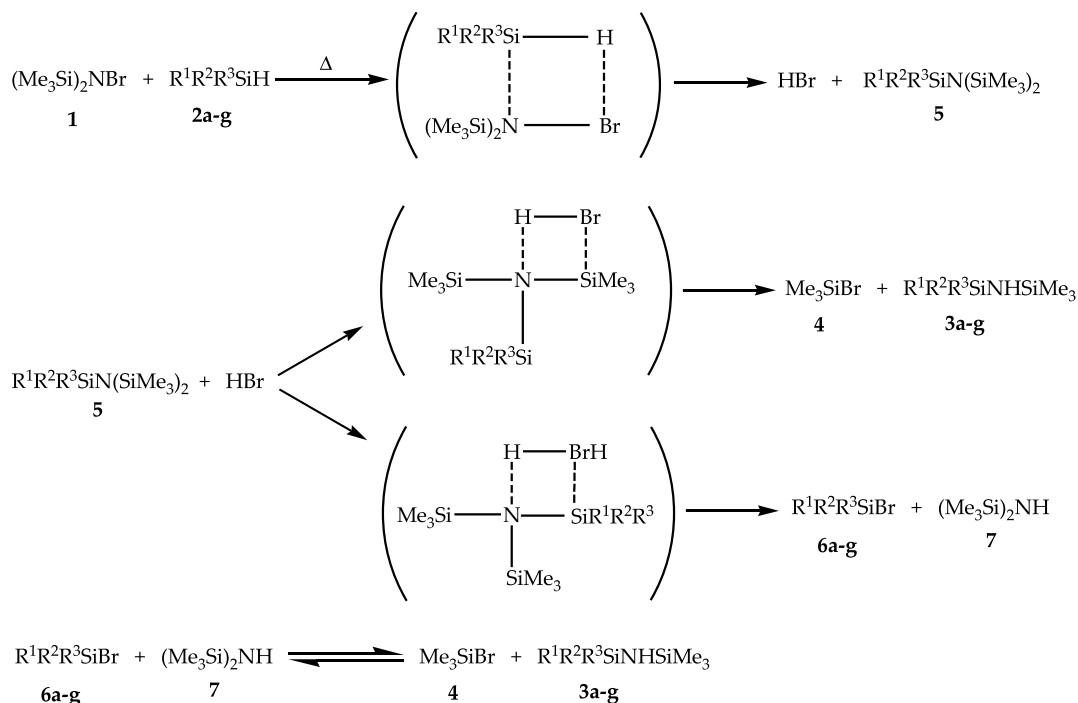
Radicals escaping the recombination in the F-pair in Scheme 2 diffuse into the bulk and bear negatively polarized Me₃Si-protons. Indeed, as above, the multiplicity factor μ , the difference of radical g -factors, Δg , and the sign of HFI constant A of Me₃Si-protons are all positive, whereas the escape recombination factor ε is negative ($\varepsilon = (-)$), therefore, the product of these factors $\mu \times \varepsilon \times \Delta g \times A = (+) \times (-) \times (+) \times (+)$ is negative and corresponds to emission (E) of Me₃Si-protons (see Section 3 for more details). These negatively polarized $(\text{Me}_3\text{Si})_2\dot{\text{N}}$ radicals are capable to react with initial N-bromohexamethyl disilazane **1** and abstract the bromine atom. Therefore, chemical exchange between $(\text{Me}_3\text{Si})_2\dot{\text{N}}$ and **1** (Scheme 2) is a most likely explanation of negative polarization transfer to the Me₃Si-protons of **1** (δ 0.25 ppm, Fig. 1). Thus, the above analysis of CIDNP effects fully confirms the sequence of the radical steps suggested in Scheme 2. It is necessary to emphasize that observed CIDNP effects favor fully radical mechanism of the photoinduced interaction of **1** and **2a–g** in cyclohexane since both $(\text{Me}_3\text{Si})_2\dot{\text{N}}$ and $\cdot\text{Br}$ free radicals are formed only under the photoinitiation. This conclusion is also supported by the observation that no products are formed when the reaction mixture in cyclohexane is kept in the dark.

2.2. Smooth bromination of silyl hydrides by N-bromohexamethyl disilazane

As opposed to the reaction in cyclohexane, the interaction in benzene starts after mixing of reagents (**1** and **2a, b, d–g**) and completes in 15–30 min. Higher yields of asymmetric disilazanes **3a, b, d–g** (see Table 1) could be explained by the assumption that the reaction under study is bimolecular and involves the formation of four-centered activated complex (Scheme 3) [12]. Decay of the complex results in HBr and the substituted trisilazane **5**, however, as it has been mentioned earlier, the latter is unstable in the presence of HBr [11]. Interaction of HBr with asymmetric trisilazane **5** is dependent on the mutual orientation of the reagents and should result in disilazanes **3** and **7** and substituted bromosilanes **4** and **6** (Scheme 3).

Of note, an attempt of the fractionated separation of the reaction products resulted in isolation of asymmetric disilazanes **3 a–g** only. Neither bromotriorganosilanes **6 a–g**, nor bromotrimethylsilane **4** were isolated from the reaction mixture. It is reasonable to assume that reaction products of two pathways of the decomposition of two four-centered activated complexes formed by **5** and HBr (mixture of **4** and **3 a–g**, and **6 a–g** and **7**; Scheme 3) are in equilibrium, and isolation of the most volatile Me₃SiBr (**4**) (b.p. 79 °C) would shift this equilibrium towards asymmetric disilazanes **3 a–g**.

To unravel the factors which control the solvent influence on the reaction mechanism of bromination of silyl hydrides **2 a–g** by N-bromohexamethyl disilazane **1** we have explored the capability of benzene to form the complex with one of the reagents. However, this assumption appears to be ungrounded, since the maximum of the UV-absorption band of **1** (342–345 nm) remains unchanged in benzene, cyclohexane, or methylene chloride. Similarly, Si–H vibration frequency, $\nu(\text{Si–H})$ of **2 a–f** is also independent of the solvent variation. But the value of the stretching vibration frequency of Si–H in **2g** is sensitive to variations of the dielectric constant and other relevant characteristics of the solvents [13,14]. In solvents with different polarity, measurable high-frequency shift of $\nu(\text{Si–H})$ has been observed, as compared to cyclohexane, e.g., in benzene, this high-frequency shift of $\nu(\text{Si–H})$ in **2g** is 5 cm⁻¹ [14].



Scheme 3. Formation and decay of four-centered activated complexes in smooth bromination of silyl hydrides by N-bromohexamethyl disilazane.

To clarify the nature of the interactions underlying the observed effects we have compared the IR-spectra (in the region from 2000 to 2300 cm^{-1}) of **2g** in solvents of different polarity/polarizability, including in benzene and in cyclohexane. As a quantitative characteristic of solvent properties, we used the Kamlet–Taft parameter π^* which reflects the capability of a solvent to participate in non-specific interactions [15,16]. Table 2 shows the correlation between Kamlet–Taft parameter π^* and Si–H vibration frequency $\nu(\text{Si–H})$ of Cl_3SiH in various solvents.

Fig. 2 shows the linear fit of $\nu(\text{Si–H})$ in Cl_3SiH as a function of Kamlet–Taft parameter π^* which follows the correlation Eq. (1):

$$\nu(\text{Si–H}) = (2250.8 \pm 0.8) + (9.2 \pm 0.8) \times \pi^* \quad (1)$$

This allows to suggest that measurable high-frequency shift of $\nu(\text{Si–H})$ in the IR-spectrum of Cl_3SiH **2g** in benzene is stipulated by non-specific intermolecular interaction between **2g** and the solvent.

If the solvent influence on the reaction mechanism in the case of other silyl hydrides **2a–f** is of the same nature, *i.e.*, it is due to the variations of solvent's capability to enter nonspecific interactions, one might expect that the reaction of **2a–f** with **1** in a series of solvents would follow different pathways reflecting the changes in the Kamlet–Taft parameter π^* . To this end, we have compared the reaction of **1** and dimethylphenylsilane PhMe_2SiH (**2a**) in cyclohexane, carbon tetrachloride, benzene, and methylene chloride. Indeed, in cyclohexane ($\pi^* = 0$), the reaction occurs only under UV-irradiation, in benzene ($\pi^* = 0.59$) and in methylene chloride ($\pi^* = 0.82$) the products are formed after the mixing of reagents. However, in CCl_4 ($\pi^* = 0.28$), which is intermediate in this

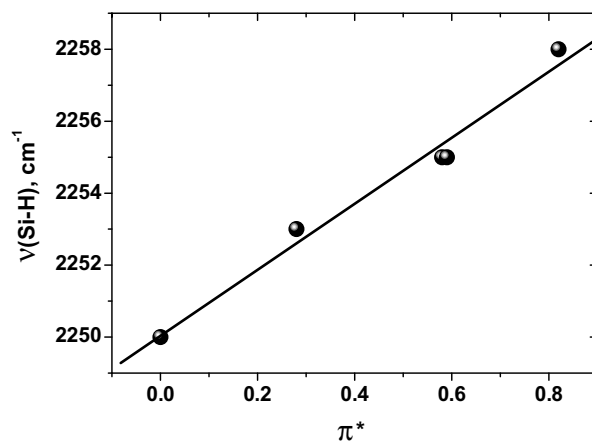


Fig. 2. Linear fit ($R^2 = 0.99$, $\text{SD} = 0.48$) of the dependence of $\nu(\text{Si–H})$ in Cl_3SiH on Kamlet–Taft parameter π^* in a series of solvents (data taken from Table 2).

series of solvents somewhere between cyclo- C_6H_{12} and benzene, only a weak warming-up of the reaction mixture is observed, and the formation of measurable amounts of the reaction products requires the UV-irradiation.

These results confirm the assumption that in the present case, nonspecific interactions of the reagents with a solvent affect the reaction mechanism. One of the possible explanations could involve solvent-mediated differences in stabilization effects for suggested four-centered activation complexes. As for the possible

Table 2
Correlation between Kamlet–Taft parameter π^* and Si–H vibration frequency $\nu(\text{Si–H})$ of Cl_3SiH in various solvents.

Solvent	Stretching vibration frequency $\nu(\text{Si–H})$ in 2g , cm^{-1}	Kamlet–Taft parameter, π^*
Cyclohexane	2250	0.00
Carbon tetrachloride	2253	0.28
Chloroform	2255	0.58
Benzene	2255	0.59
Methylene chloride	2258	0.82

involvement of free radicals, we failed to detect any CIDNP effects when the reagents are mixed in benzene, and this supports the conclusion that reaction of **1** and **2a–g** in benzene is nonradical. Still, it is necessary to emphasize that unusual drastic solvent effects in the brominations using N-bromohexamethyl disilazane **1** require further in-depth exploration.

3. Experimental

Well-established and approved standard approaches were used to synthesize N-bromohexamethyl disilazane ($\text{Me}_3\text{Si}_2\text{NBr}$ (**1**) [17] and silyl hydrides **2a–g** [18]. Their measured physical constants (b.p., n_D^{20} and δ (ppm) in the NMR spectra, etc.) were in full agreement with the reference data, and GLC-determined purity grade was not lower than 99.5%.

For GLC analyses, we employed Tsvet 500 gas-liquid chromatograph (heat conductivity detector, He flow, glass column 3 mm \times 4 mm, 10% PMS-1000 on a Chromaton N-AW-HMDS, 0.20–0.25 mm grain). NMR spectra of the initial reagents and the reaction products were recorded in CDCl_3 ("Izotop") using BRUKER DPX-400 NMR spectrometer (400 MHz ^1H operating frequency) with TMS or HMDS added as an internal standard. Spectral characteristics of the compounds under study were measured using IR-spectrometer Specord 75 and UV-spectrometer Specord UV-Vis.

3.1. Bromination reaction and product analysis

Equimolar mixture of N-bromohexamethyl disilazane ($\text{Me}_3\text{Si}_2\text{NBr}$ (**1**) and silyl hydride $\text{R}^1\text{R}^2\text{R}^3\text{SiH}$ (**2a–g**) after degassing in accordance with "freeze-pump-thaw" technique was irradiated by the full light of UV lamp (DRT-400, 400 W, Hg) during 10 h in a sealed glass tube. Reaction product was isolated by fractional distillation and identified by means of NMR spectra recorded using BRUKER DPX-400 NMR-spectrometer. Following reaction products were isolated and characterized.

1,1,1,3,3-Pentamethyl-3-phenyl disilazane, $\text{PhMe}_2\text{SiN(H)SiMe}_3$ (**3a**): b.p. 87 °C/2 mm, n_D^{20} 1.4861; δ (^1H , CDCl_3 , TMS): 0.03 (s, 9H, SiMe_3), 0.32 (s, 6H, SiMe_2), 7.3–7.35, 7.55–7.6 (m, 5H, SiPh).

1,1,1,3-Tetramethyl-3,3-diphenyl disilazane, $\text{Ph}_2\text{MeSiN(H)SiMe}_3$ (**3b**): b.p. 163 °C/9 mm, n_D^{20} 1.5435; δ (^1H , CDCl_3 , TMS): 0.06 (s, 9H, SiMe_3), 0.66 (s, 3H, SiMe), 7.36–7.43, 7.58–7.66 (m, 10H, SiPh₂).

1,1,1-Trimethyl-3,3,3-triphenyl disilazane, $\text{Ph}_3\text{SiN(H)SiMe}_3$ (**3c**): b.p. 187 °C/1 mm, n_D^{20} 1.5823; δ (^1H , CDCl_3 , TMS): –0.04 (s, 9H, SiMe_3), 7.23–7.30, 7.62–7.67 (m, 15H, SiPh₃).

1,1,1-Trimethyl-3,3,3-triethoxy disilazane, $(\text{EtO})_3\text{SiN(H)SiMe}_3$ (**3d**): b.p. 68 °C/2 mm, n_D^{20} 1.4078; δ (^1H , CDCl_3 , TMS): 0.10 (s, 9H, SiMe_3), 1.22 (t, 7 Hz, 9H, $\text{CH}_3\text{--CH}_2\text{--}$), 3.81 (q, 7 Hz, 6H, $\text{CH}_3\text{--CH}_2\text{--}$).

1,1,1,3,3-Pentamethyl-3-dimethylsiloxy disilazane, $\text{Me}_2\text{HSiO-SiMe}_2\text{N(H)SiMe}_3$ (**3e**): b.p. 46 °C/12 mm, n_D^{20} 1.4185; δ (^1H , CDCl_3 , TMS): 0.08 (s, 9H, SiMe_3), 0.1 (s, 6H, SiMe_2), 0.18 (d, 3 Hz, 6H, SiMe_2), 4.71 (m, 3 Hz, 1H, SiH).

1,1,1,3,3-Pentamethyl-3-dimethylsilylamino disilazane, $\text{Me}_2\text{H-SiN(H)SiMe}_2\text{N(H)SiMe}_3$ (**3f**): b.p. 92 °C/2 mm, n_D^{20} 1.4566; δ (^1H , CDCl_3 , TMS): 0.16 (s, 9H, SiMe_3), 0.19 (d, 3.5 Hz, 6H, SiMe_2), 0.29 (s, 6H, SiMe_2), 4.71 (m, 3.5 Hz 1H, SiH).

1,1,1-Trimethyl-3,3,3-trichloro disilazane, $\text{Me}_3\text{SiN(H)SiCl}_3$ (**3g**): b.p. 40 °C/2 mm; δ (^1H , C_6D_6 , TMS): 0.09 (s, 9H, SiMe_3), 2.23 (s, 1H, NH).

3.2. ^1H CIDNP effects and their analyses

^1H CIDNP spectra were detected using JEOL JNM FX90Q high-resolution NMR-spectrometer (90 MHz ^1H operating frequency) equipped with special in-house device for the irradiation of the samples directly in the probe of the spectrometer. Irradiation

was carried out in standard Pyrex NMR tubes with the full light of high-pressure Hg lamp (DRSh-1000, 1 kW). A thermal filter was used to prevent the heating of the sample. GS/MS analysis of the irradiated reaction mixture was carried out by means of Agilent Technologies HP6890N/HP5973N mass-spectrometer using the capillary columns HP-5MS with step-gradient heating from 50 °C to 150 °C.

The analysis of CIDNP effects was carried out using existing empirical rules [19]. Sign of net CIDNP effect (I) observed in high magnetic fields is defined by the product of multiplication of the following parameters:

$$\Gamma = \mu \times \epsilon \times \Delta g \times A$$

where μ reflects the multiplicity of the radical pair precursor, (+) for triplet and uncorrelated F-pair, and (–) for singlet precursor, ϵ is (+) for in-cage and (–) for escape recombination products, Δg is the sign of the difference between g-factor of the radical with polarized nucleus (proton in our case) and g-factor of the partner radical in a radical pair, A defines the sign of hyperfine interaction constant of the polarized nucleus (proton, in our case) in the radical under study. The sign of I 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 protons in the product resulting from recombination (ϵ is (+)) of uncorrelated radical pair (F-pair, μ is (+)), and if this group belonged to a radical with the g-factor which is smaller than that of the partner radical in the radical pair (Δg is (+)), and if the sign of hyperfine interaction for this particular group in the radical is positive (A is (+)), then the multiplication gives

$$\begin{aligned} \mu \times \epsilon \times \Delta g \times A &= (+) \times (+) \times (+) \times (+) \\ &= (+) \text{ that is, absorption (A),} \end{aligned}$$

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

4. Conclusion

Reaction of N-bromohexamethyl disilazane ($\text{Me}_3\text{Si}_2\text{NBr}$ (**1**) with substituted silyl hydrides $\text{R}^1\text{R}^2\text{R}^3\text{SiH}$ (**2a–g**) results in asymmetric disilazanes $\text{Me}_3\text{SiNHSiR}^1\text{R}^2\text{R}^3$ (**3a–g**) and bromotrimethyl silane Me_3SiBr (**4**). The simplicity of the reaction under study and high yield of the final reaction products favour this reaction as a convenient preparative method for asymmetric disilazanes.

Photoinitiated interaction of **1** with silyl hydrides in cyclohexane leads to major reaction product, the symmetric silazane **7**. Using ^1H CIDNP method, it has been demonstrated that photoinitiated reaction between **1** and **2a–g** in cyclohexane includes a series of consecutive radical steps involving disilazanyl ($\text{Me}_3\text{Si}_2\text{N}^\cdot$) and silyl $\text{R}^1\text{R}^2\text{R}^3\text{Si}^\cdot$ radicals.

Important result of the present paper is the observation of two formation mechanisms of asymmetric silazanes in different solvents – photoinduced radical reaction in cyclohexane and soft bromination when the reagents are mixed in benzene. Thus, we have found very convenient reaction which allows to perform a comparative study of chirality effects in radical and nonradical reactions resulting in identical products. This issue will be a subject of our further investigations.

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