NMR, IR, and ESR spectroscopic investigation of reaction of α-silylamines with carbon tetrachloride

Nataliya F. Lazareva[a]*, Tamara I. Vakul'skaya[a] and Igor M. Lazarev[a]

This paper reports about high reactivity of α-silylamines in the reaction with CCl_4. Unlike Et_3N, α-silylamines rapidly react with CCl_4 upon irradiation with daylight to form α-silylamine hydrochloride salts in 92–98% yields. The influence of structure of α-silylamines and solvent on the degree of conversion was displayed. The interaction of α-silylamines with CCl_4 was studied by NMR, ESR, and IR spectroscopy. C-centered radicals of α-silylamines were detected by ESR spectroscopy with spin traps (MNP, ND, and PBN) in reaction mixtures in CH_3CN and C_6H_6 and it show the radical character of this reaction. Both CH_3CN and C_6H_6 serve as solvents as well as reagents for this reaction. A mechanism of an interaction between α-silylamines and CCl_4 is discussed. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: α-silylamines; carbon tetrachloride; C-centered radical of α-silylamine; ESR; NMR; IR-spectroscopy
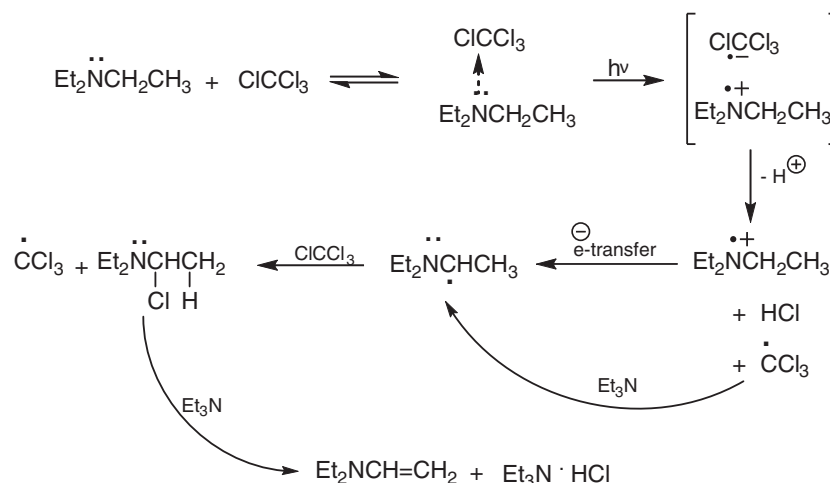
INTRODUCTION

Carbon tetrachloride (CCl_4) is widely used in various fields of organic chemistry as a solvent[1,2] and, in particular, for investigation of properties of amines.[3–7] The first data about instability of solutions of amines in CCl_4 appeared in the middle of the previous century. Their solutions in glass vessels turned yellow upon storage, the amine hydrochlorides precipitated, and chloroform was formed.[8,9] When studying this phenomenon using the methods of UV, IR, and NMR spectroscopy and X-ray analysis, the formation of weak charge–transfer complexes of amines with polyhalogenomethanes was found.[10–23] It was assumed that complexation of amine with $C(Hal)_4$ (Hal = halogen) was due to the interaction of the lone pair on the nitrogen atom of the amine with the σ^*-orbital of the C—Hal bond.[20] According to the X-ray date, in crystalline amine–polyhalogenomethane complexes, the nitrogen atoms of the amine molecule coordinate with the halogen atoms, forming discrete donor–acceptor pairs.[16,17,21] Of special interest is chemical transformation of these complexes under the action of light which is the reason of instability of the amine solutions in CCl_4. Investigation of the mechanism of this reaction started practically simultaneously with studying the process of complex formation of amines with polyhalogenomethanes.[8,11,14,18] Such factors as UV irradiation, addition of salts of transition metals, and effect of the glass surface facilitate the reaction.[14,15,22,23] Kosover was the first who offered the mechanism of the reaction between Et_3N and CCl_4[11] (Scheme 1). By now, it is unequivocally established that in weak complexes of amines with tetrahalogenomethanes upon irradiation in the near UV field the electron transfers from the amine to tetrahalogenomethane with the formation of the pair of the radical cation of amine and the radical anion of tetrahalogenomethane (reference [18] and references therein). The latter usually undergoes irreversible degradation to afford the halogen anion and the radical $\cdot CHal_3$.[18,24–26]

The radical cations of arylamines were identified by characteristic absorption spectra and the paths of their further transformations were studied.[18] Application of the CIDNP method proved the radical nature of the reaction between CCl_4 and triethylamine.[27–29] Enhanced absorption in the CIDNP spectra was observed for the signals of chloroform and terminal olefinic protons of diethylvinylamine during photolysis of the charge–transfer complex Et_3N—CCl_4 in acetonitrile or methanol. This suggests the formation of the radical pair $Et_2NC'HCH_3$—$'CCl_3$ in the first stage of the reaction and confirms the earlier proposed mechanism for the reaction of triethylamine with CCl_4[11] (Scheme 1). Diethylvinylamine is an extremely unstable compound which polymerizes to afford a product with the system of conjugated bonds. The formation of this polymer may account for the coloring of the reaction mixture.[28,29]

Recently, we have found that the induction period of the reaction of 1-dialkylaminomethylsilatranes $R_2NCH_2Si(OCHRCH_2)_3$ N (R = Me, $(CH_2)_5$) with CCl_4 upon irradiation with the daylight is 0.2 h, whereas for the reaction of Et_3N with CCl_4 under similar conditions this period reaches 96–144 h.[30] The yields of the corresponding salts $[R_2N^+HCH_2Si(OCHRCH_2)_3N]Cl^-$ and $[Et_3NH^+]Cl^-$ are 42–48% (20 h) and 0.5% (164 h) accordingly. We have assumed that such a drastic difference in the reactivity of 1-dialkylaminomethylsilatranes and triethylamine is caused by the abnormally high basicity of the exocyclic nitrogen atom[31] due to a strong electron donating inductive effect of

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Scheme 1. The mechanism of the reaction between Et_3N and CCl_4 proposed by Kosover[11]

silatranylmethyl group ($\sigma^* = -2.24$[32,33]). Introduction of the second silatranylmethyl group to the nitrogen atom results in a substantial increase of its basicity in N-methyl-N, N-bis-(silatranylmethyl)amine $MeN[CH_2Si(OCH_2CH_2)_3N]$[31] and, as a consequence, in its reactivity.[34,35] So far, the reaction of this compound with CCl_4 was not studied. In this work, we discuss the results of investigation of α-silylamines in their reaction with CCl_4 obtained by IR, ESR, and NMR spectroscopy. As the objects for this goal, α-silylamines $RR'NCH_2SiX_3$ **1–7** and, for comparison, triethylamine **15** were chosen.

RESULTS AND DISCUSSION

Compounds **1–7** reacts with CCl_4 when exposed to daylight at room temperature in benzene, acetonitrile, or in an excess of CCl_4 resulting in the formation of the amine hydrochloride products **8–14** as shown in Scheme 2.

In all cases the induction period does not exceed 0.5–15 min depending on the solvent and the structure of α-silylamine. The yield of products **8–14** in various solvents as a function of the reaction time are given in Table 1. The yield of **8–14** in CCl_4 as the solvent is less than 50% after 24 h and a large amount of poorly soluble, colored products is formed, that agrees well with our previous results.[30] We failed to identify the colored products from the reaction mixtures with compounds **5–7**. However, from the reaction mixtures with silatranes **1–4**, extraction of the solid residue obtained after removal of excess CCl_4, with boiling methylene chloride afforded the mixtures of salts **8–11** with 1-chlorosilatrane. As observed from the ^1H NMR spectra, the

methylene chloride extracts from these reactions contained 7–12% of 1-chlorosilatrane, it was determined by integration of the intensities of the CH_2N and CH_2O proton signals of the silatrane ring. In acetonitrile the reaction with CCl_4 was completed in 36–72 h and the yield of salts **8–14** was almost quantitative. The compounds **1–7** react with CCl_4 in benzene more slow than in acetonitrile. After the same period, the yields of compounds **8–14** in acetonitrile were much higher than in benzene. For example, the yield of compound **8** in CH_3CN and C_6H_6 after 2 h comprises 41 and 18% accordingly. The yield of by-products in these solvents is slight. The structure of the α-silylamine has a pronounced effect on the yield provided that all other things are equal. On the one hand, the structure of the silyl group is of importance, since the yield of the silatranyl-containing products **8–11** is higher than **12–14**. On the other hand, an important factor is the number of silylmethyl groups at the nitrogen atom. Thus, introduction of a second silylmethyl group, irrespective of its structure, increases the yield provided that all other things are equal. For example, the yield of compounds **8** and **9** containing two silatranylmethyl groups is higher than that of compounds **10**, **11**, containing only one such group. Similarly, the yield of the compound **13**, containing two trimethylsilylmethyl groups is larger than that of compound **12** containing only one such group.

In the presence of hydroquinone or in the dark the reaction of compound **1** with CCl_4 proceeds extremely slowly. Unlike the above α-silylamines, the mixture of triethylamine **15** with CCl_4 is stable when exposed to light during several days. However, upon the UV irradiation of this mixture triethylamine hydrochloride **16** is formed as soon as in 2 h.
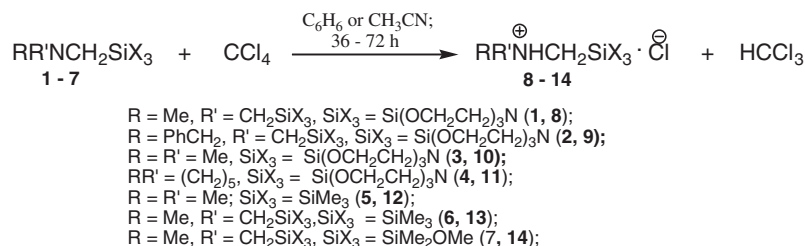
Scheme 2. The reaction of α-silylamines **1–7** with CCl_4

Table 1. Yields of $[RR'NH^+CH_2SiX_3]Cl^-$ is function of the reaction time

Solvent	t, h	Yields of $[RR'NH^+CH_2SiX_3]Cl^-$							
		8	**9**	**10**	**11**	**12**	**13**	**14**	**16**[c]
CCl$_4$	2	11	12	8	9		7	2	traces
CCl$_4$	8	27	26	17	19	5	16	14	
C$_6$H$_6$	2	18	17	11	12	2	11	8	
C$_6$H$_6$	8	34	36	29	28	12	23	17	
C$_6$H$_6$	24	57	58	39	41	26	35	29	
C$_6$H$_6$	48	91				61			
CH$_3$CN	2	41	39	29	31	8	25	19	3
CH$_3$CN	8	76	79	67	69	17	51	44	
CH$_3$CN	24	89	90	79	80	29	78	71	
CH$_3$CN	24	7[a]							
CH$_3$CN	24	3[b]							
CH$_3$CN	36	97	94	98	92			94	
CH$_3$CN	48						96		
CH$_3$CN	72					98			

[a] The reaction mixture was kept in the dark.
[b] Hydroquinone was added to CH$_3$CN before mixing.
[c] UV irradiation.

The structures of products **8**–**14** were assigned by multinuclear NMR spectroscopy (Tables 2–4). A downfield shift of the signals of the NCH$_3$ and NCH$_2$Si groups in the ^{1}H NMR spectra of **8**–**14** with respect to the starting compounds **1**–**7** (Table 2) is indicative of the quaternization of the nitrogen center.[35,36] The proton resonance of the NCH$_2$Si group in compound **8**, **9** represents an AB quartet ($J_{AB} = 14.0$ Hz) and the proton resonance of the NCH$_2$C (a skeleton of silatranes) is an AB quartet, where each component is split into a triplet with a vicinal coupling constant ($J_{AB} = 12.5$ Hz, $^3J = 6.2$ Hz). Protonation of the nitrogen atom in N-methyl-N,N-bis(silatranylmethyl)amine **1** and **2** produces a prochirality[37] of NCH$_2$Si groups and these methylene protons becomes diastereotopic.[38] Diastereotopic atoms of hydrogen have a various chemical environment (Scheme 3) and differ by chemical and physical properties. In particular, methylene protons are anisochronous, that is, these atoms have a various chemical shift in the ^{1}H NMR spectra.[39,40] The typical example of prochiral molecule with diastereotopic hydrogen atoms is 2-butanol MeCH$_A$H$_B$CH(OH)Me.[38]

The ^{1}H NMR monitoring of the reaction mixture of compounds **1**, **3**, and **7** with CCl$_4$ in acetonitrile shows that the singlet signal of chloroform ($\delta = 7.28$ ppm) appears in the spectra within 1 h. Its intensity depends on the structure of the α-silylamine (**1** > **3** > **7**) and increases in time (Fig. 1).

IR spectroscopy was employed to investigate the reaction of compounds **1** and **3** with CCl$_4$ in acetonitrile. These two compounds were chosen for the IR study because of the presence of the NMe group in the molecules. The symmetric stretching vibration band v(C—H) of the NCH$_3$ group at 2750–2760 cm^{-1} was chosen as an analytical marker.[41] This band is absent in the ammonium salts MeRR'R''N$^+$Cl$^-$, so that the decrease of its intensity allows to determine the degree of the quaternization reaction. The intensity of the NMe band in the IR spectrum of the reaction mixture of compound **3** with CCl$_4$ decreases non-uniformly (Fig. 2). The spectrum remains practically unchanged within 10 min after mixing of the reagents, that is in line with the existence of the induction period in this reaction.[30] Then, during 8 h, it gradually decreases to 30% of the original value. No

Table 2. ^{1}H NMR data for the α-silylamines R$_2$NCH$_2$SiX$_3$ and the corresponding ammonium salts $[R_2NH^+CH_2SiX_3]Y^-$ in CD$_3$CN

	R$_2$NCH$_2$SiX$_3$				$[R_2NH^+CH_2SiX_3]Y^-$		
	δ, ppm				δ, ppm		
No.	R–N	N–CH$_2$–Si	SiX$_3$	No.	R–N	N–CH$_2$–Si	SiX$_3$
1	2.17 (s)	1.89 (s)	2.83 (t)	**8**	2.83 (s)	2.17 ($J_{AB} = 14.0$ Hz)	3.03 ($J_{AB} = 12.5$ Hz, $^3J = 6.2$ Hz);
			3.79 (t)		5.79 (NH$^+$)	2.39	3.82 (t)
2	3.52 (s)	1.94 (s)	2.77 (t)	**9**	4.18 (d) ($^3J = 5.38$ Hz)	2.16 ($J_{AB} = 14.43$ Hz) 2.36	2.95 (t)
	7.15 (m)		3.79 (t)		7.44 (m) 6.02 (NH$^+$)		3.74 (t)
3	2.20 (s)	1.63 (s)	2.78 (t)	**10**	2.86 (s)	2.13 (s)	2.96 (t)
			3.74 (t)		2.57 (NH$^+$)		3.82 (t)
4[a]	1.59 (m)	1.80 (s)	3.77 (t)	**11**[a]	1.57 (m)	2.17 (s)	3.83 (t)
	2.41 (m)		2.80 (t)		3.05 (m)		2.91 (t)
					10.15 (NH$^+$)		
5	2.22 (s)	1.85 (s)	0.06 (s)	**12**	2.60 (s)	2.31 (s)	0.19 (s)
					9.83 (NH$^+$)		
6	2.10 (s)	1.82 (s)	0.18 (s)	**13**	2.74 (s)	2.60 (s)	0.24 (s)
					11.55 (NH$^+$)		
7	2.17 (s)	1.86 (s)	0.02 (s)	**14**	2.70 (s)	2.61 (s)	0.24 (s)
					10.78 (NH$^+$)		3.36

[a] Solvent CDCl$_3$.

Table 3. $^{13}C\{^1H\}$ data for the α-silylamines $R_2NCH_2SiX_3$ and the corresponding ammonium salts $[R_2NH^+CH_2SiX_3]Y^-$ in CD_3CN

| | $R_2NCH_2SiX_3$ | | | | $[R_2NH^+CH_2SiX_3]Y^-$ | | |
| | δ, ppm | | | | δ, ppm | | |
No.	R–N	N–CH$_2$–Si	SiX$_3$	No.	R–N	N–CH$_2$–Si	SiX$_3$
1	54.51	47.46	50.96 57.26	**8**	53.52	46.69	50.07 57.02
2	62.16 129.39 129.49 128.41 139.74	57.34	50.91 58.26	**9**	60.49 129.87 131.23 133.46	49.95	50.25 57.91
3	53.02	50.37	51.69 58.12	**10**	51.11	48.58	50.29 57.19
4[a]	24.76 26.77 59.01	51.42	51.92 58.43	**11**[a]	22.18 25.27 58.87	49.86	50.12 57.27
5	49.74	43.40	−1.49	**12**	48.69	40.98	0.63
6	56.76	50.94	−1.21	**13**	52.94	46.36	−0.57
7	55.33	50.66	−1.16	**14**	52.73	48.15	−0.78 50.59

[a] Solvent $CDCl_3$.

Table 4. ^{29}Si data for the α-silylamines $R_2NCH_2SiX_3$ and the corresponding ammonium salts $[R_2NH^+CH_2SiX_3]Y^-$ in CD_3CN

No.	$R_2NCH_2SiX_3$	No.	$[R_2NH^+CH_2SiX_3]Y^-$
1	−81.53	**8**	−84.99
2	−81.11	**9**	−85.04
3	−75.31	**10**	−81.52
4[a]	−73.23	**11**[a]	−82.39
5	−1.55	**12**	−1.78
6	−1.86	**13**	−0.94
7	−1.99	**14**	−0.95

[a] Solvent $CDCl_3$.

Figure 1. The dependence of the change of the integrated intensity of chloroform signal with time in reaction mixtures **1** (Δ) [or **3** ($\bullet$) or **7** (o)]–CCl_4–CH_3CN

induction period was observed in the reaction of compound **1** with CCl_4. The band at 2753 cm^{-1} started to gradually drop immediately after mixing of the solutions of compound **1** and CCl_4 in acetonitrile to reach 20% of its starting value after 8 h (Fig. 2a). The excess of CCl_4 has no effect on the degree of conversion of the starting α-silylamine. The absorption bands of the silatranyl group are retained in the products **8**, **10** (Table 5),

whereas the ν(C—H) bands of the NCH_3 group at 2700–2800 cm^{-1} are absent. New bands appearing at 2400–2700 cm^{-1} belong to the stretching vibrations of the N$^+$—H group. The IR spectra of compounds **8**, **10** are identical to those of
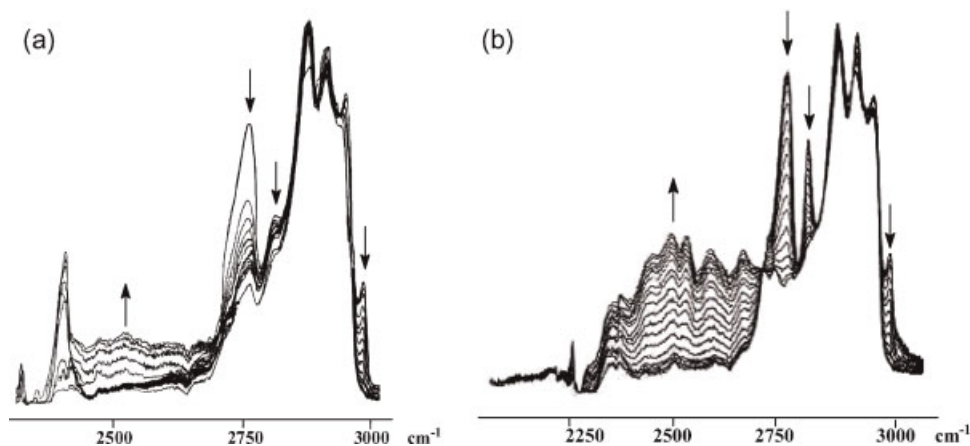

Scheme 3. Nonequivalence of diastereotopic hydrogen atoms in methylene group of compounds RCH_AH_BEXYZ (E = C, N)

Figure 2. The change of IR spectra of the reaction mixture with time (0–8 h) (a) **1**–CCl_4; (b) **3**–CCl_4 (solvent CH_3CN)

hydrochlorides of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine and *N*,*N*-dimethyl(silatranylmethyl)amine.[30,35]

As noted above, the reaction of α-silylamines with CCl_4 proceeds in the light and is retarded by hydroquinone, that is indicative of its radical character and is in compliance with the known data on the reactions of organic amines with poly-halogenomethanes.[18] According to Scheme 1, the reaction of amine with CCl_4 begins with the formation of the (radical anion of

CCl_4-radical cation of amine) pair which is further transformed into the α-radical of amine and $^\bullet CCl_3$. Based on the pathway shown in Scheme 1, we anticipate the observation of some of these intermediates by ESR spectroscopy. Earlier, the use of this method allowed us to identify the formation of the radical cation of amine **1** in its reaction with $AgNO_3$.[35] However, no signals in the ESR spectra were detected in the reaction mixtures of compounds **1**, **2**, and **4** with CCl_4. This may be due to small

Table 5. Characteristic[a] IR frequencies for the amines, $Me_nN[CH_2Si(OCH_2CH_2)_3N]_{3-n}$ [$n = 1$ (**1**), $n = 2$ (**3**)] and the corresponding hydrochloride salts **8** and **10**

Compounds				
1	**8**	**3**	**10**	Assignment
585 (m)	589 (m)	585 (m)	580 (m)	$\nu_s(SiO_3)$
633 (m)	638 (m)	621 (m)	628 (m)	
655 (m)	659 (m)			
790 (s)	791 (s)	779 (m)	783 (s)	$\nu_s(SiOC)$
815 (s)	814 (s)	815 (s)	791 (s)	
914 (m)	916 (m)	911 (m)	907 (m)	$\nu(CC)$, $\nu(CO)$, $\nu(CN)$
940 (m)	943 (m)	938 (m)	930 (m)	
		945 (m)		
1090 (vs)	1085 (vs)	1090 (s)	1077 (s)	$\nu_{as}(COSi)$
1115 (s)	1113 (s)	1101 (s)	1110 (s)	
		1124 (s)		
1277 (m)	1274 (m)	1276 (m)	1273 (m)	$\delta(NCC)$
	2498 (w)		2480 (m)	$\nu(N^+H)$
	2531 (w)		2520 (m)	
	2605 (w)		2590 (w)	
	2636 (w)		2700 (w)	
	2674 (w)			
2755 (m)		2755 (m)		$\nu((CH_3)N)$, $\nu((CH_3)_2N)$
		2808 (m)		
2880 (m)	2882 (m)	2873 (m)	2878 (m)	$\nu(CH_2,CH_3)$
2937 (m)	2939 (m)	2914 (m)	2930 (m)	
2950 (m)	2977 (m)	2934 (m)	2950 (m)	
		2969 (m)		
		2994 (w)		

[a] s, strong; m, medium; w, weak; vs, very strong.
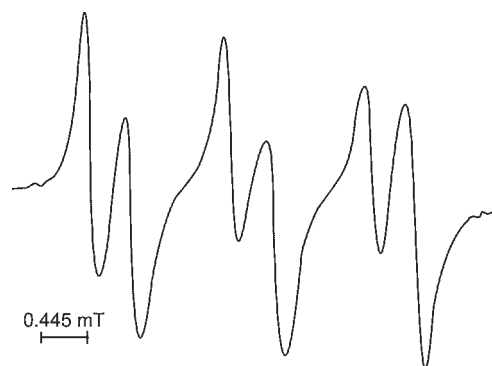
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Figure 3. ESR spectrum of the reaction mixture **4**–CCl_4–C_6H_6 with MNP after 2 h
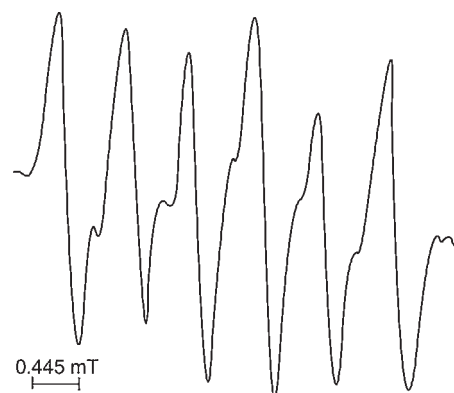

Figure 4. ESR spectrum of the reaction **1**–CCl_4–C_6H_6 in the presence of ND after 1 h

concentration of the complex between the amine and polyhalogenomethane[18] that would give rise to low concentration of the intermediates formed upon its decomposition. A short lifetime of the intermediates could also affect the detection of the ESR signal. With this in mind, we made an attempt to study the reaction between α-silylamine and CCl_4 using the ESR spin-trapping method.[42] 2-Methyl-2-nitrosopropane (MNP), nitrosodurol (ND), and α-phenyl-*N-tert*-butylnitron (PBN) are well-known spin traps[43] widely used for trapping of unstable carbon-centered radicals[44] including $^\bullet CCl_3$. We used all of these spin traps assuming that their different selectivity[45] will allow us to register all radicals formed in the reactions of α-silylamines with CCl_4. Indeed, in the ESR spectra of the reaction mixtures of compounds **1**, **2**, **4**, and **15** with CCl_4 in benzene in the presence of MNP the signals of different intensity were registered. The ESR signals obtained from the reaction of **4** with CCl_4 in C_6H_6 in the presence of MNP were relatively broad triples of doublets (Fig. 3) caused by the interaction of the unpaired electron with one nucleus with spin 1 (nitrogen) and one nucleus with spin ½ (proton). Their characteristics are given in Table 5. With regard to the literature data,[44] the observed signals belong to the spin adducts of MNP to the C-centered radicals of the type $R'R''N^\bullet CHR$. Computer simulation of the spectra has shown, that their asymmetry is due to superposition of the triplet signal from t-$Bu_2NO^\bullet$ radical. MNP eliminates the *tert*-butyl radical which is trapped with another molecule of MNP to give t-$Bu_2NO^\bullet$ radical.[42,44] The intensity of the latter considerably increases in time, and it is easily identified by the value of the hyperfine splitting constant $a_N = 1.556$ mT. No other spin adducts with MNP were found.

In the ESR spectra of the reaction mixtures of **1** and **4** with CCl_4 and ND the overlapping signals of the spin adducts from the two radicals are observed (Figs. 4–6). The value of the hyperfine splitting constant of these triplets of doublets (Table 6) is typical for spin adducts of ND with carbon-centered radicals containing proton in the α-position to the radical center,[44] which are formed by deprotonation of radical cations of amines (Scheme 1). The second signal appears on the background of the main triplet of doublets (Table 6, Fig. 4) and its characteristics are determined from the spectrum with high resolution after 12 h (Figs. 5 and 6) and coincides with those of the spin adduct, ND/$^\bullet Ph$.[44] This assignment was corroborated by the fact that when benzene was replaced by deuterobenzene the signal of the spin adduct ND/$^\bullet C_6D_5$ was split to a triplet from the nitrogen center with a constant of 1.0 mT. Further splitting to a doublet on the α-proton
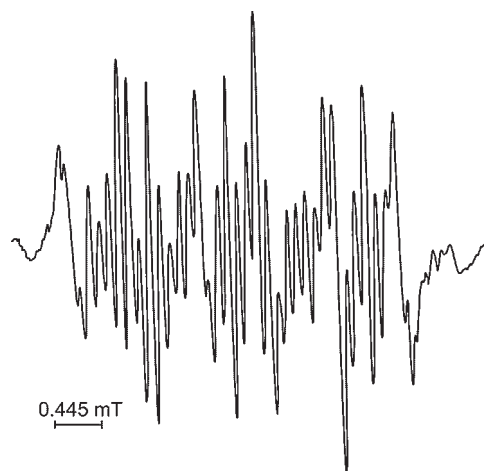

Figure 5. High-resolution ESR spectrum of the reaction mixture **2**–CCl_4–C_6H_6 in the presence of ND after 12 h
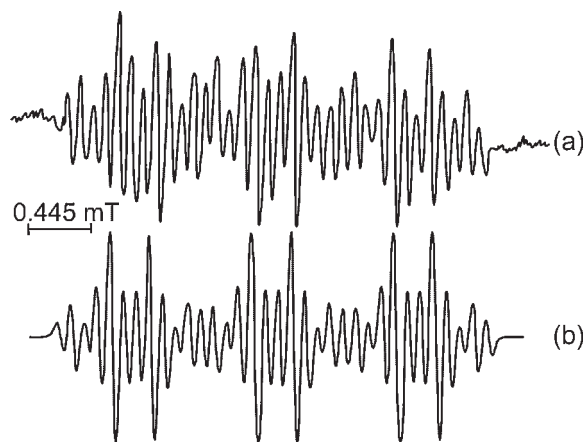

Figure 6. ESR spectrum of spin adduct ND/$^\bullet Ph$ observed in the reaction mixtures of compounds **1**, **2**, **4**, and **15** with CCl_4 in benzene in the presence of ND: (a) experimental after 24 h and (b) simulated ESR spectrum

Table 6. ESR spectral parameters for the spin adducts formed in the reaction of amines **1**, **2**, **4**, and **15** with CCl_4 in the presence of spin traps

		Spin trap								
		MNP			ND[a]			PBN		
Amine	Solvent	a_N, mT	$a_{H(1)}$, mT	g-factor	a_N, mT	$a_{H(1)}$, mT	g-factor	a_N, mT	$a_{H(1)}$,[b] mT	g-factor
1	CCl_4/C_6H_6	1.378	0.456	2.0067	1.234	0.648	2.0054	1.420	0.220 (0.110)	2.0062
								1.388	0.156 (0.088)	2.0063
	CCl_4, C_6D_6				1.236	0.650	2.0054			
	CCl_4				1.233	0.644	2.0054	1.388	0.156 (0.100)	2.0063
2	CCl_4, C_6H_6	1.365	0.478	2.0066	1.222	0.600	2.0055	1.420	0.218 (0.110)	2.0062
								1.388	0.156 (0.088)	2.0063
	CCl_4				1.333	0.622	2.0055	1.388	0.156 (0.100)	2.0063
4	CCl_4, C_6H_6	1.398	0.447	2.0064	1.244	0.623	2.0055	1.422	0.222 (0.088)	2.0062
								1.388	0.156 (0.088)	2.0063
	CCl_4, C_6H_6, $h\nu$[c]							1.388	0.156 (0.088)	2.0063
	CCl_4, C_6D_6	1.377	0.445	2.0064	1.249	0.622	2.0055	1.388	0.156 (0.067)	2.0063
	CCl_4	1.377	0.445	2.0064	1.248	0.624	2.0055	1.388	0.156 (0.088)	2.0063
	CCl_4, $h\nu$[c]				1.288	0.622	2.0055	1.388	0.156 (0.088)	2.0063
15	CCl_4, C_6H_6	1.360	0.410	[d]	1.400	0.666	2.0054	1.388	0.156 (0.100)	2.0063
	CCl_4	1.355	0.440	[d]	1.400	0.666	2.0054	1.388	0.156 (0.100)	2.0063

[a] Multicomponent signal of the spin adduct of ND with phenyl radical identified by the value of hyperfine splitting constant a_N 10.11; $a_{H(3)}$ 2.78; $a_{H(2)}$ 0.95;[47] and g = 2.00614[46] is overlapped with the main triplet of doublets in all cases in the system CCl_4–C_6H_6 in the presence of ND.
[b] The width of a line is given in brackets.
[c] After UV irradiation for 5–7 min in a quartz cell.
[d] One more signal was observed (not identified).

was not manifested in the spectrum because the hyperfine constant for deuterium is seven times less than that for proton.

In the ESR spectra of the reaction mixture of **4**/CCl_4 in benzene in the presence of PBN (Fig. 7) similar signals to those of the mixture of the spin adducts PBN/•CCl_3 and PBN/•C_6H_5[46] were observed. Because of strong overlapping the signals cannot be separated in the X-range. Indeed, computer simulation has shown the observed ESR spectra to be superposition of the two triplets of doublets which belong to spin adducts of PBN with trichloromethyl and phenyl radicals (Table 6). In the course of the reaction the intensity of the signal of the spin adduct PBN/•CCl_3 is increased so that the contribution of PBN/•C_6H_5 becomes negligible. In the absence of benzene, only the spin adduct PBN/•CCl_3 is registered in the ESR spectra (Table 6, Fig. 7b).

α-Silylamines belong to a large group of compounds XCH_2M with heteroatoms X = O, S, or N in the geminal position to the element of the 14th group (M = Si, Ge, and Sn), which possess unique reactivity and unusual spectroscopic properties.[48–52] Various models are invoked to explain the nature of this α-effect.[53–58] Amines having the silyl group in the α-position, $R_2NCH_2SiX_3$, show an increased basicity as compared with their carbon analogs and their ionization potential is lower than that of trialkylamines.[59–62] According to the literature,[53,63] the increase of the energy of the lone pair of heteroatom (and, hence, low ionization potential) is due to destabilizing four-electron geometrically dependent interaction of the lone pair with the σ(C—Si) orbital,[64] whereas the radical cation center on the heteroatom is stabilized by hyperconjugation of the half-

occupied lone pair orbital with the σ^*(C—Si) orbital. The increased basicity and the low ionization potential are the key properties of α-silylamines, which are responsible for the drastic difference of their reactivity from that of organic amines. If it is
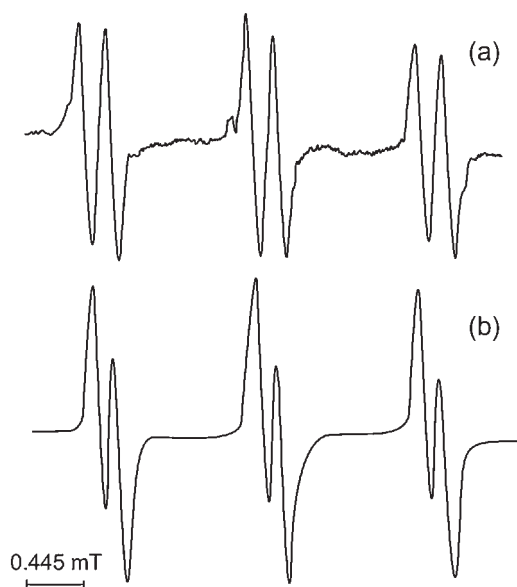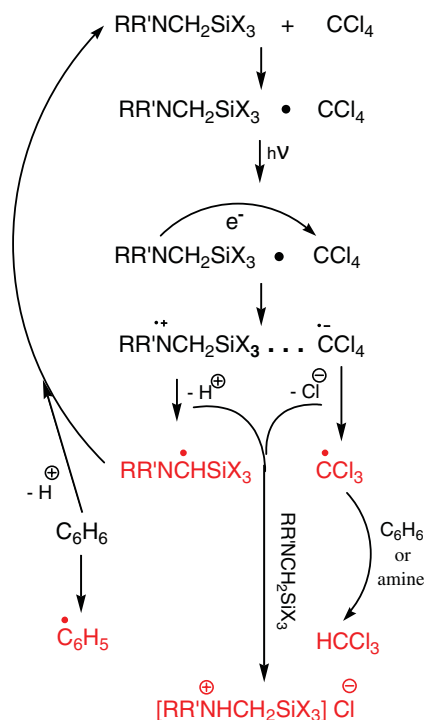

Figure 7. ESR spectra of the reaction mixture **4**–CCl_4–C_6H_6 in the presence PBN: (a) 2 h and (b) 36 h

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granted that the formation of complex of amine and CCl_4 occurs due to interaction of the lone pair of nitrogen atom with the $\sigma^*(C—Cl)$-orbital[20] it must depend on the basicity of the nitrogen atom. The low ionization potential of the α-silylamines provides an explanation for their propensity to single electronic transfer reactions under the conditions of photochemical initiation with the formation of the corresponding radical cations.[65,66] A similar process takes place in the complex $RR'R''N—CCl_4$ under the action of daylight. The experiments showed that the reactivity of the studied α-silylamines **1–7** depends on the number and structure of organosilicon substituents being changed in the order **1 >> 2 > 3 >> 4 > 6 > 7 > 5**. Both the basicity and the potential of oxidation of amines are governed by their structure, that is, by inductive and steric effects of the substituents at the nitrogen atom.[67–72] The donor inductive effect of the $CH_2Si(OCH_2CH_2)_3N$ group is much larger than that of the CH_2SiMe_3 group (σ_I are -0.36 and -0.05, respectively),[32,33,73] that makes the exocyclic nitrogen atom of α-silatranylamines more basic than in α-trialkylsilylamines. The degree of pyramidalization of the nitrogen atom is another major factor determining the electron donating ability of its lone pair.[72,74] Apparently, a steric effect of silatranyl group caused the change of degree of pyramidalization of nitrogen atom. It is not excluded, that the sum of these two factors provides higher reactivity of α-silatranylamines **1–4** in comparison with α-silylamines **5–7**.

The electron transfer in weak complexes of amines with polyhalogenomethanes gives rise to the formation of the pair of the radical cation of amine and radical anion of CCl_4.[18] Unfortunately, we failed to detect these intermediates when studying the reaction mixtures $RR'CH_2NSiX_3—CCl_4$ by ESR. Yet, the use of the spin traps allowed us to register the C-centered radicals of α-silatranylamines. Under the same conditions, we also detected the trichloromethyl radical formed by degradation of the radical anion of CCl_4. The $^\bullet CCl_3$ radical forms chloroform molecule that proved by NMR spectroscopy. These results agree well with the data known for organic amines.[18] One of the most probable paths of degradation of the radical cation of tertiary amine is the process of α-deprotonation with the formation of the C-centered radical.[75–80] Despite of a great deal of publications devoted to the problem of degradation of radical cations of amines, so far there is no distinct understanding of the process of deprotonation. Apparently, it depends on the structure and basicity of amine and includes several elementary steps. The direction of degradation of radical cations of α-silylamines $RR'NCH_2SiMe_3$ is determined by the unique structure of the $SiCH_2N$ fragment and depends on the structure of the substituents and the nature of the solvent used.[81–83] In aprotic solvents (acetonitrile) α-deprotonation predominates whereas desilylation proceeds mainly in polar protic solvents (methanol). The reaction of compounds **1–7** with CCl_4 in benzene or acetonitrile results in the formation of the corresponding amines hydrochlorides **8–14** in close to quantitative yields. This may be only if the solvent takes part in the reaction as an H-donor to radical $^\bullet CH(NRR')SiX_3$ to return the starting amine to the reaction cycle. Acetonitrile is known to be hydrogen atom donor.[84,85] The radical $^\bullet CH_2CN$ formed after expulsion of hydrogen atom from acetonitrile can dimerize to give succinonitrile. Indeed, we observed the appearance of new signals in the ^1H (2.76 ppm) and ^{13}C (14.8 and 119.6 ppm) NMR spectra of the reaction mixtures of compounds **1** and **3** with CCl_4 in acetonitrile solution after 1 day. The formation of phenyl radical was observed when studying the reactions of α-silylamines with CCl_4 in benzene as a solvent by the

use of ESR spectroscopy. These facts corroborate the participation of solvents (benzene and acetonitrile) as donors of hydrogen atom in these reactions. Apparently, the C-centered radicals of α-silylamines eliminate hydrogen atom from the molecule of the solvent to recover the starting α-silylamine with the transfer of the radical center to the rest of the solvent molecule. This allows to explain quantitative transformation of α-silylamines into the corresponding hydrochlorides in aprotic solvents. The above analysis allows to assume the following tentative mechanism of the reaction of α-silylamines with CCl_4 in aprotic solvents (Scheme 4. The products and intermediates identified by us in this reaction are given in red).

When excess of CCl_4 is used as a solvent the yields of silylamines do not exceed 50%. The main reason of the decrease of the yield is that in the absence of the H-donor solvent the C-centered radicals of α-silylamines are stabilized by recombination or decomposition. The products of the recombination of a radical $RR'NC^\bullet HSiX_3$ were not found in the reaction mixtures of compound **1–7** with CCl_4. We have found that 1-chlorosilatrane is present among the products of the reaction of compounds **1–4** with excess of CCl_4. The insoluble, yellowy–brown solid residues of polymeric products were obtained after extraction of compounds **8–14** from the reaction mixtures. The absorption bands at 1660–1685 cm^{-1} in IR spectra of polymeric products belong to $NC=C$ groups (polyconjugated bonds). This result coincides with data which have been received at the studying of the by-products of oxidation reaction of amines.[28] The element analysis showed the high contents of chlorine in the polymers (30–65%). Apparently, one of the ways of stabilization of the radical of α-silylamine may be the process of desilylation with the formation of $ClSiX_3$ and polymeric products containing the $NC=C$ group (Scheme 5). Probably, the reaction proceeding at the mixing of the α-silylamine with an excess of CCl_4 is more complex

Scheme 4. A possible mechanism for the reaction between α-silylamines and CCl_4 (C_6H_6 solvent)

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Scheme 5. A possible mechanism for the reaction between α-silylamines and excess of CCl_4

than is represented by Scheme 5. However, the scheme provides an explanation for the formation of the 1-chlorosilatrane in the reaction mixture.

CONCLUSION

The results presented in this account demonstrate the higher reactivity of the α-silylamines **1–7** with CCl_4 compared to Et_3N. Unlike Et_3N, the interaction of α-silylamines with CCl_4 begins within few minutes after their mixing upon the irradiation of the daylight. This reaction has a radical character and it is in compliance with the known data on the reactions of organic amines with polyhalogenomethanes. C-centered radicals of α-silylamines were detected by ESR spectroscopy in reaction mixtures in CH_3CN and C_6H_6. The α-silylamines hydrochlorides are formed with high yield, if the reaction was running in these solvents. If the reaction was running in an excess of CCl_4, then the yield of α-silylamines hydrochlorides decreases significantly and simultaneously with the increasing of yield of by-products. The investigation of the reaction mixtures by spectroscopy confirmed that the solvents (CH_3CN and C_6H_6) were also reagents for the reaction. Probably, the radicals of α-silylamines break loose an H atom from solvent. This possibility is absent, if the reaction run in excess of CCl_4 and a decay of radicals of α-silylamines takes place with the formation of a great quantity of by-products.

Finally, CCl_4 is relatively inert organic liquid, which is used extensively as a solvent in spectroscopic investigations, in synthetic organic chemistry and in extraction processes. However, it is necessary to remember at use of CCl_4 that this solvent sometimes can react with a dissolved compound.

EXPERIMENTAL

General procedure of the interaction of α-silylamines 1–7 with CCl_4

α-Silylamine (0.1 mmol) was dissolved in 3 mL of a solvent in the Schlenk tube. The solution was degased and was added the 0.15 mmol (an excess) of the previously degassed CCl_4 by the syringe. This mixture was degassed once again and was stirred on a magnetic stirrer at room temperature and upon irradiation with the daylight with time which indicated in Table 1. After a solvent was removed on the rotor evaporator, a solid residue was drying in the vacuum. The crude product was then purified by the recrystallization.

It is necessary to note, that the reaction CCl_4 with the compounds **5–7** is extremely sensitive in the presence of a trace of H_2O at a reaction mixture. If this reaction is to be carried out in the wet solvents preferentially the formation of the products of the cleavage Si—C bond is observed.

N-Methyl-N,N-bis(silatranylmethyl)amine hydrochloride (8)

The reaction required 36 h for full completion of the reaction. The yield of the crude product was 97% and the yield after recrystallization (chloroform–hexane, 1:1) was 86%. Anal. calcd. for $C_{15}H_{32}ClN_3O_6Si_2$: C 40.76; H 7.30; N 9.51; found: C 40.64; H 7.11; N 9.60.

N-benzyl-N,N-bis(silatranylmethyl)amine hydrochloride (9)

The reaction required 36 h for full completion of the reaction. The yield of the crude product was 94% and the yield after recrystallization (chloroform–hexane, 1:1) was 81%. Anal. calcd. for $C_{21}H_{36}ClN_3O_6Si_2$: C 48.68; H 7.00; N 8.11; found: C 48.89, H 7.31, N 8.06.

N-(silatranylmethyl)diamine hydrochloride (10)

The reaction required 36 h for full completion of the reaction. The yield of the crude product was 99% and the yield after recrystallization (chloroform–hexane, 1:1) was 88%. Anal. calcd.

for $C_9H_{21}ClN_2O_3Si$: C 40.21; H 7.87; N 10.42; found: C 40.37; H 8.05; N 10.63.

N-(silatranylmethyl)piperidine hydrochloride (11)

The reaction required 36 h for full completion of the reaction. The yield of the crude product was 92% and the yield after recrystallization (chloroform–hexane, 1:1) was 83%. Anal. calcd. for $C_{12}H_{25}ClN_2O_3Si$: C 46.66; H 8.16; N 9.07; found: C 46.82; H 7.96; N 9.15.

N-(trimethylsilylmetyl)dimethylamine hydrochloride (12)

The reaction required 72 h for full completion of the reaction. The yield of the crude product was 98% and the yield after recrystallization (chloroform–hexane, 1:1) was 90%. Anal. calcd. for $C_6H_{18}ClNSi_2$: C 42.96; H 10.82; N 8.35; found: C 43.11; H 10.98; N 8.47.

N-methyl-N,N-bis(trimethylsilylmetyl)amine hydrochloride (13)

The reaction required 48 h for full completion of the reaction. The yield of the crude product was 96% and the yield after recrystallization (chloroform–hexane, 1:1) was 89%. Anal. calcd. for $C_9H_{26}ClNSi_2$: C 45.05; H 10.92; N 5.84; found: C 45.14; H 11.11; N 5.69.

N-methyl-N,N-bis(methoxydimethylsilylmetyl)amine hydrochloride (14)

The reaction required 36 h for full completion of the reaction. The yield of the crude product was 94% and the yield after recrystallization (chloroform-hexane, 1:1) was 88%. Anal. calcd. for $C_9H_{26}ClNO_2Si_2$: C 39.75; H 9.64; N 5.15; found: C 40.04; H 9.71; N 5.09.

NMR investigation of reaction compound *1*, 3, and 7 with CCl₄

Solution (1 mL) of compound **1**, **3**, or **7** in acetonitrile ($c = 0.3 \, mol \, L^{-1}$) mixed with 1 mL solution of CCl_4 in acetonitrile ($c = 0.3 \, mol \, L^{-1}$). This reaction mixture immediately transferred a NMR tube which containing a capsule with DMSO-d6. Preparation of solutions and their transfer to a NMR tube was carried out in the glovebox under inert, dry atmosphere (Ar). NMR tube exposed at room temperature and upon irradiation with the daylight with 1 h just before their submission in NMR spectrometer. NMR spectroscopic monitoring was proceeding at 2 h interval. A content of chloroform was determined by integration of the intensities of proton signals *H*—C of chloroform and N—*Me* of α-silylamine.

IR investigation of reaction compound 1, 3 with CCl₄

Solution (3 mL) of compound **1** or **3** in acetonitrile ($c = 0.3 \, mol \, L^{-1}$) mixed with 3 mL solution of CCl_4 in acetonitrile ($c = 1.6 \, mol \, L^{-1}$). This reaction mixture immediately transferred a cell KBr ($d = 0.0096$ cm). Preparations of solutions and transfers to a cell were carried out in the glovebox under an inert, dry atmosphere (Ar). IR spectroscopic monitoring was achieved in the spectral range of 3100–2000 cm^{-1}.

The experimental technique in ampoule ESR

The sample procedure of the preparation of the ESR ampoule was made in the glovebox, which was shading. Before the preparation of the sample, the glassware was wrapped in black paper. To a 1 mL solution of the α-silylamine (1.5 mmol L^{-1}) was added a spin trap (MNP, ND, or PBN).[39] This solution was seated in the ampoule by a syringe and was degassed by several freeze-thaw cycles. Then the equimolar amount of the previously degassed CCl_4 was added to the mixture of α-silylamine with the spin trap by the syringe. This mixture was degassed once again by several freeze-thaw cycles and the ampoule was sealed. The ampoule was thawed and the solution was mixed carefully. The ampoule was irradiated by the daylight for 5 min just before their submission in the resonator of an ESR spectrometer.

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