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(*N*-Trifluoromethanesulfonyl)sulfimides of Linear and Cyclic Organosilicon Sulfides

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Abstract—The reaction of sodium salt of *N*-(chloro)trifluoromethanesulfonamide with linear and cyclic five- and six-membered organosilicon sulfides was studied and their first *N*-trifluoromethanesulfonyl-substituted imides were synthesized. The results are compared with the data on the reaction of the same substrates with chloramine B. The distinctly pronounced stabilizing effect of a highly electronegative trifluoromethanesulfonyl group was observed, which decreased the reactivity of *N*-trifyl-substituted sulfimides with respect to electrophilic reagents and increased their stability. Mass spectra of isomeric cyclic organosilicon *N*-trifluoromethanesulfonyl-substituted sulfimides **VII**, **X**, their acyclic analog **III**, and the product of the decomposition of the latter at the Si–C(S) bond **IV** were studied. The mechanism of formation of sulfimides in nonaqueous media is discussed.

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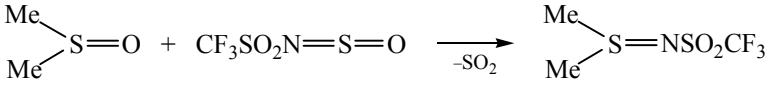
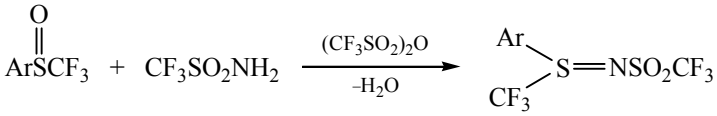
Sulfimide derivatives of organic sulfides, including cyclic ones, are well studied. They are prepared both in aprotic or in aqueous and other protic media, depending on the reagents used [1–5]. *N*-Triflyl derivatives of organic sulfimides are much less studied. Taking into account a specific reactivity of trifluoromethanesulfonamide, they are prepared either by the reaction of its *N*-sulfinyl derivative $CF_3SO_2N{=}S{=}O$ with dimethylsulfoxide [Eq. (1)] [6, 7], by dehydrocondensation of aryltrifluoromethylsulfoxides with trifluoromethanesulfonamide in the presence of triflic anhydride [Eq. (2)] [8], or by oxidative imination of organic sulfides with *N*,*N*-dichlorotrifluoromethanesulfonamide [Eq. (3)] [9, 10]:


(1)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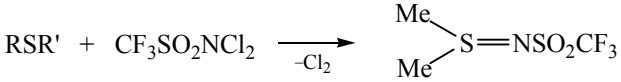

(3)

R = Ar; R' = Ar, CF_3.

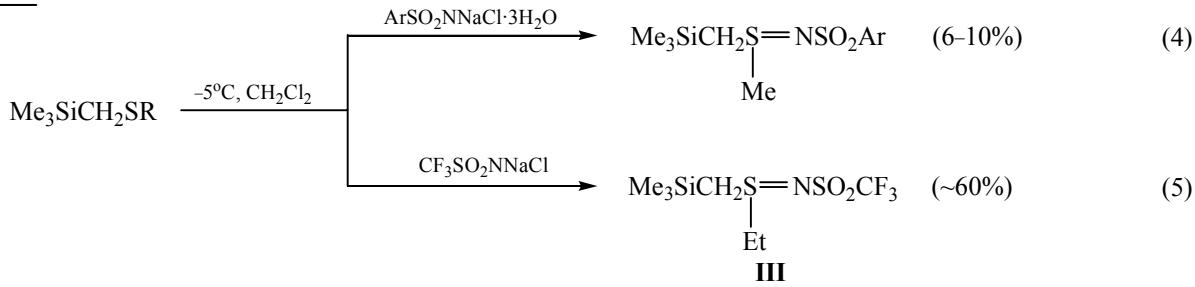
We failed to find any data in the literature concerning *N*-triflyl derivatives of cyclic sulfimides. Also, until very recently, nothing was known about *N*-triflyl derivatives of linear or cyclic organosilicon sulfimides; their first representative, 4,4-dimethyl-4-silathiane-1-(*N*-trifluoro-methanesulfonyl)sulfimide, was synthesized by us a year ago [11]. Moreover, in a recent review on diheteroatomic organosilicon heterocycles [12] only our works on the synthesis of organosilicon sulfimides [13–15] were cited.

At the same time, the introduction of the triflyl group CF_3SO_2 to the nitrogen atom in sulfimides is of considerable interest from the viewpoint of possible

stabilization of these compounds, which is especially important for organosilicon sulfimides that are hydrolytically much less stable than their organic analogs. It was reasonable to assume that the introduction of the electron-withdrawing trifluoromethanesulfonyl group would decrease the reactivity of sulfimides with respect to electrophiles and, hence, increase their hydrolytic stability. It should be mentioned that the hydrolytic stability of organosilicon sulfimides depends mainly on the relative location of heteroatoms, silicon and sulfur. We have prepared the first six-membered cyclic organosilicon sulfimides [13–15], but their five-membered analogs turned out to be unstable and decomposed with the ring opening at the Si–CH_2S bond [15]. Linear and cyclic organosilicon sulfimides are stable if the atoms of silicon and sulfur are separated by two or three CH_2 groups, and are unstable in the presence of the geminal group Si–CH_2–S [13–16]. For example, the arylsulfimide derivatives of 1,3-thiasilacyclohexane are very sensitive to the reaction conditions and can be prepared only in aprotic medium (methylene chloride) at cooling and in the presence of phase transfer catalyst, triethylbenzylammonium chloride.

In the present work we have studied the reaction of linear and cyclic organosilicon sulfides with sodium salt of *N*-chlorotrifluoromethanesulfonamide and performed qualitative comparison of the stability of the obtained *N*-triflyl-substituted sulfimides and their *N*-arylsulfonyl-substituted analogs formed in the reaction with chloramine B.

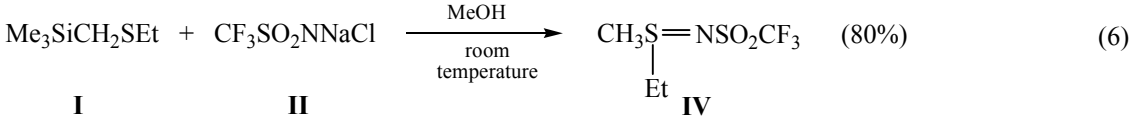
The stability of linear organosilicon *N*-arylsulfonylsulfimides with the β- and γ-location of the silicon and sulfur atoms [13, 16] makes it possible to synthesize them both in aprotic conditions (in methylene chloride), and, for example, in methanol. As distinct from that, their α-isomeric analog methyl (trimethylsilylmethyl) sulfide reacts with chloroamine B or T to form the corresponding *S*-(trimethylsilylmethyl)-*S*-methyl-*N*-(arylsulfonyl)sulfimides only under dry aprotic conditions in the presence of a phase transfer catalyst, and even then the yield is very low [16] [Eq. (4)]. We have found that the linear organosilicon sulfide, ethyl (trimethylsilylmethyl) sulfide (**I**) under similar conditions reacts with the sodium salt of *N*-chlorotrifluoromethanesulfonamide (**II**) with a much higher yield [Eq. (5)]. The product of reaction (5) is thermally stable (CCl_4, 78°C, 7 h).



R = Me ([16]), Et (present work); Ar = Ph, *p*-Tol.

The structure of product **III** is confirmed by the presence in the ^{1}H NMR spectrum of two doublets of diastereotopic protons of the $SiCH_2S$ group at 2.3 and 2.5 ppm, and two doublets of quartets of diastereotopic methylene protons of the SCH_2Me group at 3 ppm.

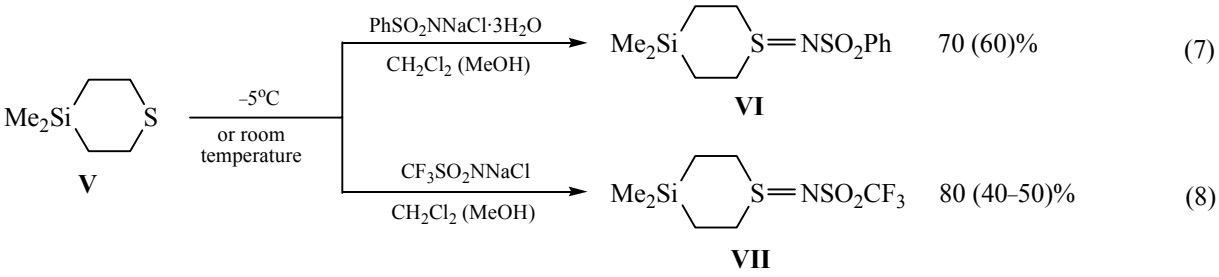
Therefore, for linear organosilicon *N*-sulfonyl-substituted sulfimides the stabilizing effect of the triflyl group CF_3SO_2 is manifested mainly in a sharp increase of the yield of the target product, from 6–10% to 60%. Moreover, *N*-triflyl-substituted sulfimide **III** withstands short-term treatment with water and the conditions of the column chromatography on silica. However, it is still impossible to synthesize it in a protic medium: when the reaction is carried out in methanol, *S*-methyl-*S*-ethyl-(*N*-trifluoromethanesulfonyl)sulfimide (**IV**), that is, the product of decomposition of **III** at the Si–C (S) bond, is formed in 80% yield as an oil, poorly soluble in organic solvents:



In the ^{1}H NMR spectrum of product **IV** a singlet of the *S*-methyl protons is observed as well as the signals of the SEt group with the coupling pattern fully identical to that in the spectrum of compound **III**.

In a similar way, compound **I** and its *S*-methyl analog react in methanol with chloramine B, to form *S*,*S*-dimethyl- [16] or *S*-methyl-*S*-ethyl-*N*-(benzenesulfonyl)sulfimides [13].

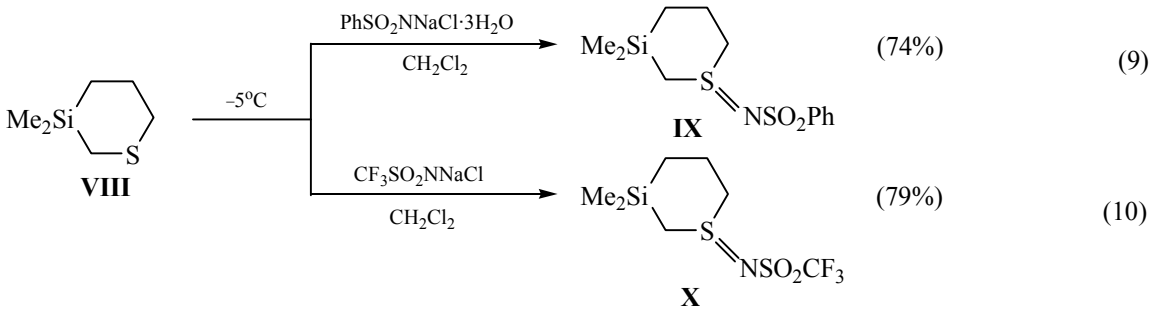
The reaction of 4,4-dimethyl-4-silathiane (**V**) with salt **II** [11] proceeds similar to its reaction with chloramine B [14]. Products **VI** and **VII** are thermally and hydrolytically stable.



The introduction of the $=NSO_2CF_3$ group to the sulfur atom results in a downfield shift and splitting of all signals in the ^{1}H NMR spectrum: the singlet of $SiMe_2$ in sulfide **V** is shifted by ~0.2 ppm and split in two signals of the axial and equatorial methyl groups, the signal of the $SiCH_2$ protons at ~1 ppm is split in two multiplets of the axial (~1 ppm) and equatorial (1.5 ppm) protons, and the signal of the SCH_2 protons at 2.8 ppm is also split in two multiplets of the axial (3.2 ppm) and equatorial (3.4 ppm) protons.

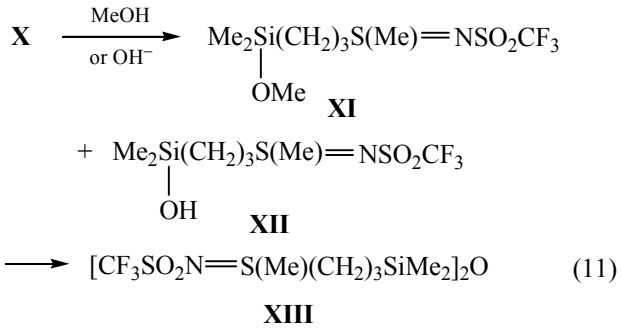
It is hard to talk about a stabilizing effect of the triflyl group by the example of reactions (7) and (8), for it is manifested here only in a slight increase of the yield of the product of the sulfimidation. Apparently, this is due to intrinsic stability of β-organosilicon sulfimides, which is supported by rather high yields of the products of the reaction performed in methanol. This is also confirmed by the results of imidation of sulfide **V** with *N*,*N*-dichlorotrifluoromethanesulfonamide $CF_3SO_2NCl_2$. Even under these much more severe conditions (40°C, presence of molecular chlorine and HCl in the reaction mixture, water treatment) ~30% of the target product **VII** is formed. Compound **VI**, judged from the ^{1}H NMR data, also remains intact after staying for 16 h in the methanol solution of HCl (pH = 3).

It was much more interesting to look for the presence of such an effect by the example of cyclic systems, containing, by analogy with the linear β-silylated sulfides, the Si–CH_2–S fragment with the geminally arranged atoms of silicon and sulfur. Therefore we studied the sulfimidation of 3,3-dimethyl-3-silathiane **VIII** isomeric to compound **V**. When carrying out the reaction in an aprotic medium, products **IX** and **X** were obtained in good comparable yields. However, the relative stability of the *N*-triflyl-substituted sulfimide **X** as compared with the *N*-arylsulfonyl-substituted analog **IX** is much higher, as proved by its much larger resistance to hydrolysis (it withstands water treatment and column chromatography on silica).



As in the case of sulfide **V**, the introduction of the $=NSO_2CF_3$ group to the sulfur atom in sulfide **VIII** results in a downfield shift and splitting of the signals of the axial and equatorial SiMe groups and the protons of the CH_2 groups. With this, the singlet of $SiCH_2S$ in sulfide **VIII** (1.7 ppm) is transformed in the product **X** into AB quartet (2.6 ppm).

Earlier we showed that, when treated with methanol or water, product **IX** decomposed with the rupture of the Si–C(S) bond and the formation of a mixture of the sulfimide derivatives of silanol, methoxysilane, and disiloxane [15]. Similar to that, according to the ^1H, ^{29}Si NMR spectroscopy data, when carrying out reaction (10) in methanol or by the action of methanol or water–alcohol alkali solution on the separately prepared product **X**, the latter is solvolytically split with the formation of the corresponding silanol, methoxysilane, and disiloxane:



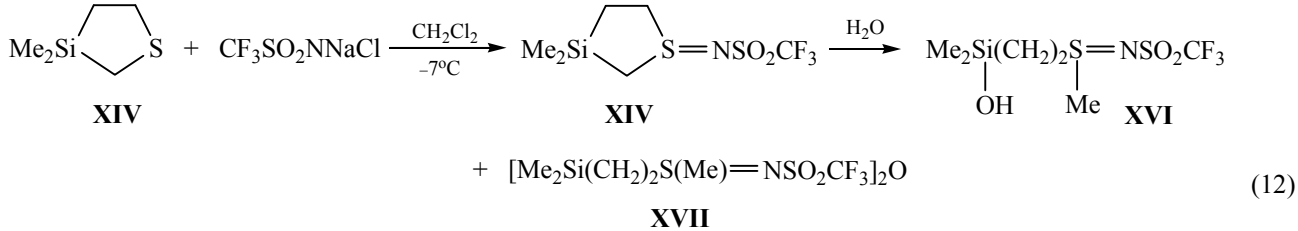
(11)

The formation of compounds **XI**, **XII** is proved by the presence in the ^{29}Si NMR spectrum of the signals at ~19 ppm and ~16 ppm, characteristic of methoxysilanes and silanols, respectively [17]. An easy transformation of sulfimide derivatives of silanols of the type **XII** into disiloxanes we demonstrated earlier for phenylsulfonyl-substituted derivatives [15], and in the present work it was confirmed spectroscopically for sulfimidation of the five-membered cyclic organosilicon sulfide (vide infra). The signals in the ^{13}C NMR spectrum of disiloxane **XIII** were assigned using the 2D{^1H–^{13}C} spectrum.

At the same time, products **IX** and **X** are thermally stable and do not undergo any changes upon reflux in CCl_4 for 7 h.

Five-membered heterocycles, *S*-functional 1,3-thiasilacyclopentanes, as we have shown earlier, are less stable than their six-membered analogs, derivatives of compounds **V** and **VIII**, and the sulfimide derivatives are the least stable as compared to other *S*-functional derivatives [15]. For example, 3,3-dimethyl-1-thia-3-silacyclopentane-1-(*N*-phenylsulfonyl)sulfimide cannot be detected in the reaction mixture by NMR spectroscopy even when performing the reaction in an aprotic medium. Only the corresponding sulfimide derivatives of silanol and disiloxane, that is, the products of the solvolytic splitting of the Si–C(S) bond, have been obtained [15].

Taking into account the stabilizing effect of the triflyl group, which is indeed the case for the linear and six-membered cyclic sulfimides with the geminal fragment Si–CH_2–S, we have examined how effective it would be for synthesis of the least stable five-membered cyclic sulfimides. It turned out that 3,3-dimethyl-1,3-thiasilacyclopentane (**XIV**) reacts with salt **II** by the following scheme:



(12)

Using the NMR spectroscopy, the target five-membered cyclic organosilicon sulfimide **XV** was identified in the reaction mixture, where its content reached 75%. However, already 2 h later, after removal of methylene chloride and addition of CCl_4 for more complete precipitation of admixtures, only trace amounts of product **XV** remained in the reaction mixture, the main components being silanol **XVI** and disiloxane **XVII**, similar to the reaction with chloramine B [15]. This is confirmed by the presence in the ^{29}Si NMR spectrum of the signals at ~16 ppm and ~8 ppm of similar intensity that are characteristic of silanols and disiloxanes, respectively [17]. The presence in the ^{19}F, ^{29}Si NMR spectra of disiloxane **XVII** of two close signals (–77.87 and –77.93; 8.14 and 8.35 ppm, respectively) in the ratio of ~1:3 is due to the presence of two

chiral centers in the molecule and the existence of the *RR*(*SS*) and *RS*(*SR*) diastereomers.

The comparison of reactions (5) and (12) reveals a substantial difference in behavior of the linear **I** and five-membered cyclic **XIV** sulfides containing the same geminal fragment Si–CH_2–S with respect to the sulfimidating reagent **II**. While the linear sulfimide **III** is isolated in 60% yield, the cyclic sulfimide **XV** is only registered in the reaction mixture. Apparently, this is due to additional destabilization of product **XV** by the ring strain.

The mechanism of imidation of sulfides by the salts of *N*-chlorosulfonamides in protic media is studied in detail; in the first stage it includes transformation of salts RSO_2NNaCl into more reactive intermediates RSO_2NHCl, which in the rate-determining step of the process react with sulfides R_2S by the mechanism of electrophilic chlorination giving rise to RSO_2NH^- and $[R_2SCl]^+$ that are rapidly converted into the final product with evolution of HCl (see, e.g., [18]). Under aprotic conditions this mechanism is impossible, although it is known that the reaction of sulfimidation under these condition proceeds in a higher yield, in particular, due to the absence of a side reaction of formation of sulfoxides [19]. The mechanism of sulfimidation in the absence of proton-donors was not discussed. It was not our task to study the mechanism of the reaction, but a priori two alternatives might be suggested. The first is based on the assumption that the substantially lower activity of RSO_2NNaCl relative to RSO_2NHCl [18] is characteristic of protic media, which sharply decreases the activity of the ionic salt form due to both nonspecific and specific solvation. In an aprotic medium these effects are much weaker, and salts RSO_2NNaCl may react as independent chlorinating agents to give with sulfides the intermediates $[R_2SCl]^+$ and RSO_2NNa^-, which after elimination of NaCl are converted into *N*-sulfonylsulfimides $R_2S{=}NSO_2R$. The second alternative is disproportionation of RSO_2NNaCl, similar to disproportionation of RSO_2NHCl to RSO_2NH_2 and RSO_2NCl_2:

$$RSO_2NNaCl \rightleftarrows RSO_2NNa_2 + RSO_2NCl_2. \qquad (13)$$

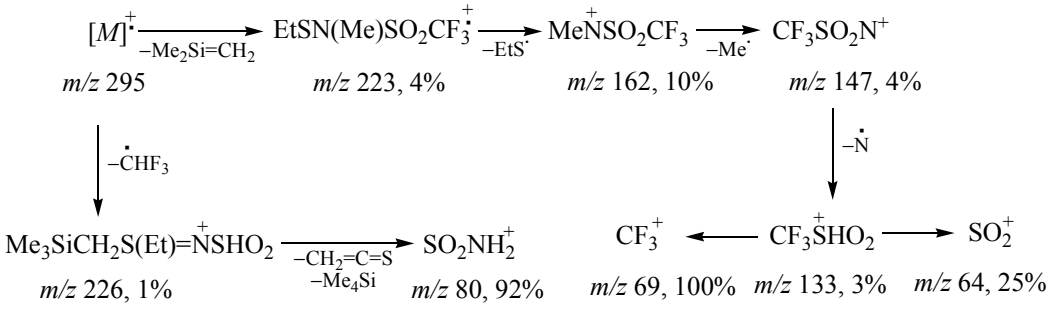
Even if Eq. (13) is strongly biased to the left, a high activity of the dichloride, which is maximum in the series of the sulfimidating reagents [18], can ensure the proceeding of the sulfimidation to give good preparative yields.

We have studied the electron impact induced decomposition of *N*-(trifluoromethanesulfonyl)-sulfimides **III, IV, VII**, and **X**. In the mass spectrum of compound **III** the peak of molecular ion (MI) is lacking, as was also noted for other sulfimines [4]. The first significant fragment peak corresponds to the rearrangement radical-ion $CF_3SO_2N(Me)SEt$ with *m/z* 223, which further eliminates radical $SEt^{\cdot}$ to give the cation $CF_3SO_2NMe^+$ with *m/z* 162. The ions of maximum intensity in the spectrum are CF_3 and SO_2NH_2 (Scheme 1).

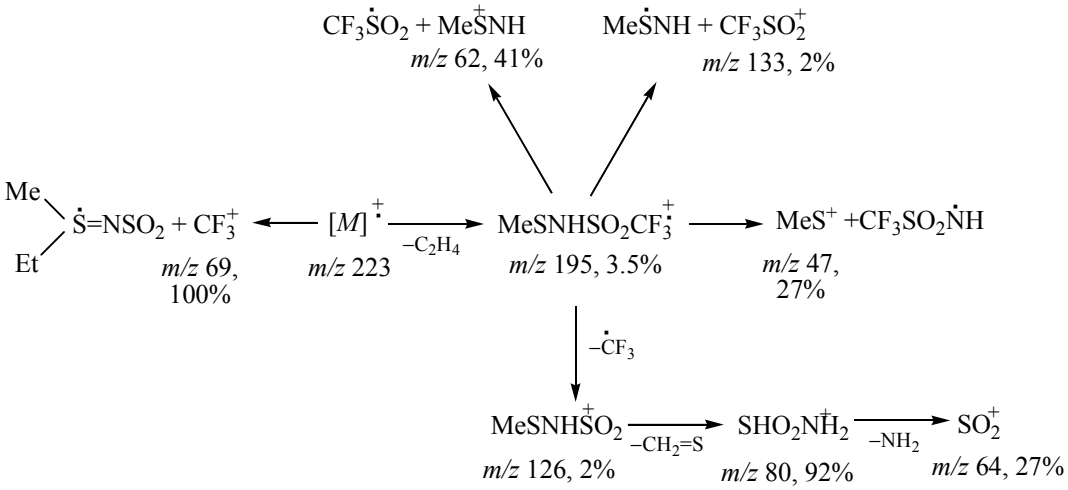
The peak of MI is also lacking in the spectrum of compound **IV**, the first fragment peak corresponds to elimination of the molecule of ethylene from MI. The main routes of further decomposition are shown in Scheme 2.

The electron impact induced decomposition of isomeric sulfimides **VII** and **X** occurs in different ways. As we have already mentioned [11], the peak of MI is lacking for compound **VII** in the regime of direct injection, but it was detected in the regime of chromatomass spectrometry. The first fragment peak is the peak of ion with *m/z* 265, corresponding to expulsion of ethylene from MI, which is in agreement with the direction of decomposition of the precursor of compound **VII**, 4,4-dimethyl-4-silathiane (**V**) [20]. Further decomposition is shown in Scheme 3.

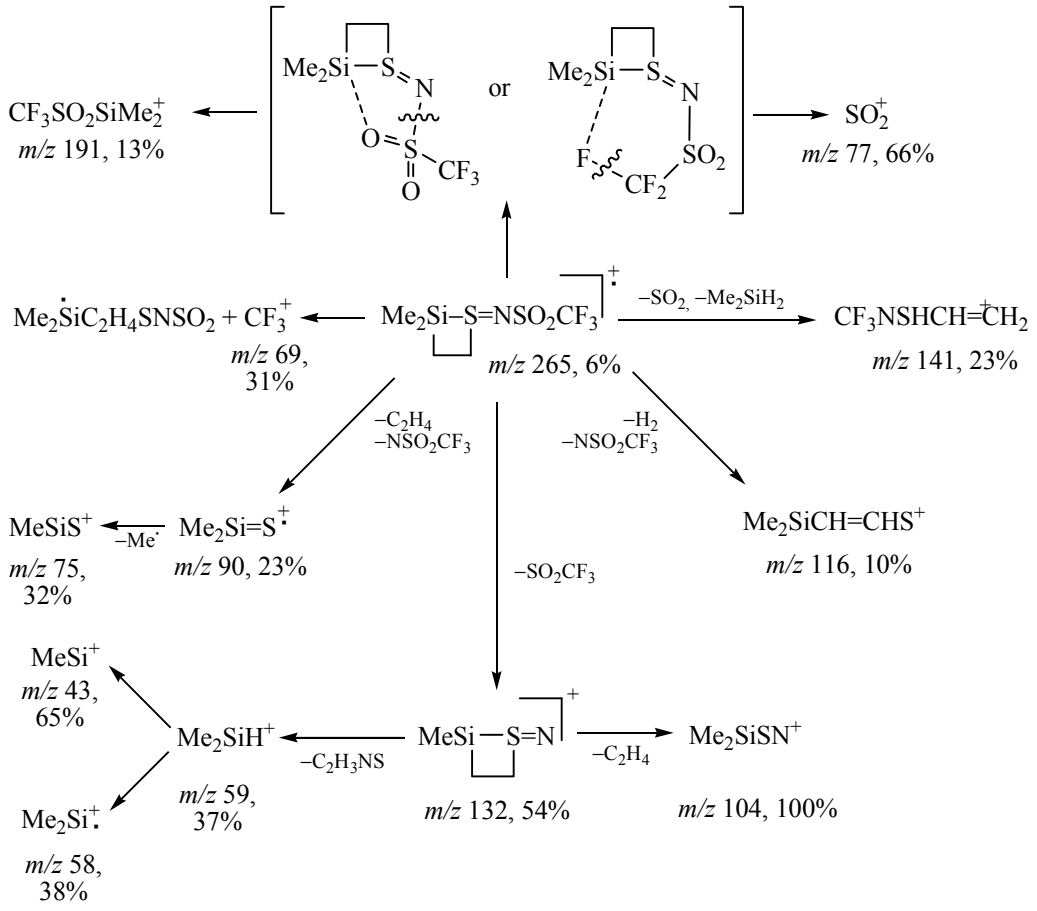
Scheme 1.



Scheme 2.

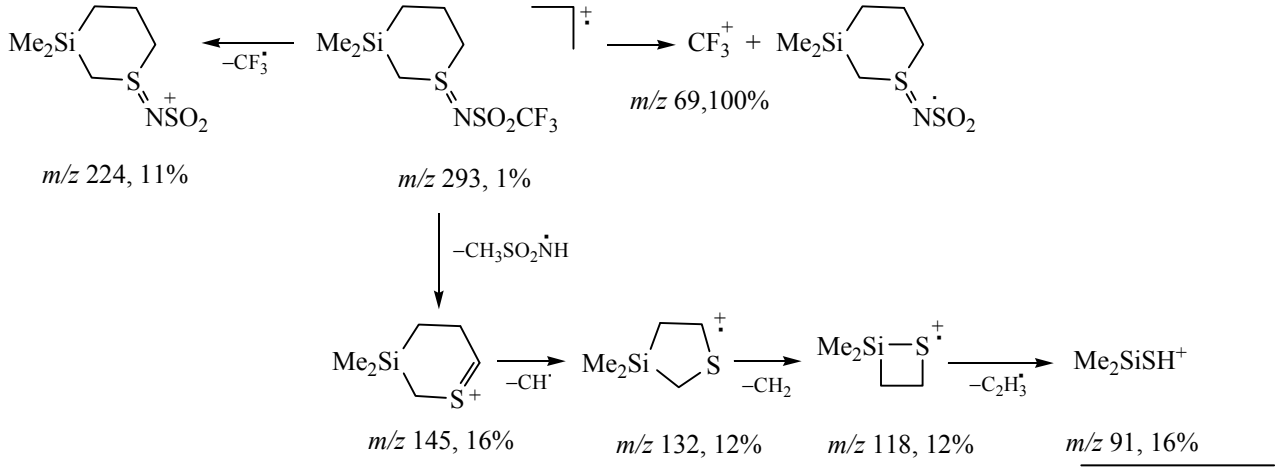


Scheme 3.



The peak of MI for sulfimide **X** also has very low intensity (1%). The first significant fragment peak with *m/z* 224 corresponds to expulsion of the trifluoromethyl radical, although the main direction of decomposition is splitting of the CF_3–S bond with localization of the charge on the CF_3 group. Further transformations are connected with fragmentation of the silathiane ring, as can be seen in Scheme 4.

Scheme 4.



EXPERIMENTAL

Melting points were determined on a Micro-Hot-Stage Polytherm A device. IR spectra were taken on a Specord IR 75 in thin layer or in KBr. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded for solutions in $CDCl_3$ (if not differently specified) on a Bruker DPX 400 spectrometer (400, 100, 376, and 79.5 MHz, respectively) with the residual protons (for ^{1}H) or the carbon atom (for ^{13}C) of the solvent as an internal standard, chemical shifts are given relative to TMS (^{1}H, ^{13}C, ^{29}Si) or CCl_3F (^{19}F). Electron impact mass spectra were obtained at 70 eV on a GCMS-QP5050A Shimadzu instrument with the quadrupole mass analyzer.

Solvents were dried and purified by standard procedures and stored over molecular sieves 4A. N,*N*-Dichlorotrifluoromethanesulfonamide and its sodium salt were prepared as described in [21]. Ethyl-(trimethylsilylmethyl)sulfide (**I**), 4,4-dimethyl-4-silathiane (**V**), 3,3-dimethyl-3-silathiane (**VIII**), 3,3-dimethyl-1,3-thiasilacyclopentane (**XIV**) were prepared by procedures described in [14, 22–24], respectively.

***S*-(Trimethylsilyl)-*S*-ethyl-(*N*-trifluoromethanesulfonyl)sulfimide (III).** To a mixture of 0.35 g of sulfide **I**, 0.027 g of triethylbenzylammonium chloride and freshly calcined zeolites in 5 ml of anhydrous CH_2Cl_2 at temperature from 0 to –4°C in an argon atmosphere 0.486 g of salt **II** was added by portions during 40 min, the reaction mixture was stirred for 1 h at 0°C and 3 h at room temperature. The solvent was removed, the residue was extracted with ether, the extract was washed with water, dried over $MgSO_4$, ether was removed to obtain 0.419 g (60%) of the crude product **III** as a white powder. The compound was purified by column chromatography on silica gel (Merck) in the system hexane, hexane–ether from 8:1 to 1:7, mp 84°C. IR spectrum, ν, cm^{-1}: 2960 (CH_2), 1310 (SO_2), 1230 (SiMe), 1200, 1165 (CF_3), 1120 (SO_2), 990 (S=N), 970 (NSO_2), 820 (CS), 595 (SO_2). ^{1}H NMR spectrum, δ, ppm: 0.29 s (9H, $SiMe_3$), 1.45 t (3H, CMe, *J* 7.4 Hz), 2.31 d (1H, $SCH^{A}Si$, *J* 13.7 Hz), 2.52 d (1H, $SCH^{B}Si$, *J* 13.7 Hz), 3.00 d.q (1H, $SCH^{A}C$, *J* 13.0, 7.1 Hz), 3.05 d.q (1H, $SCH^{B}C$, *J* 13.0, 7.2 Hz). ^{13}C NMR spectrum, δ, ppm: –1.13 (SiMe), 7.03 (CCH_3), 35.90 (SCSi), 46.36 (S*C*C), 120.29 q (CF_3, J_{CF} 323.3 Hz). ^{19}F NMR spectrum, δ, ppm: –77.71. ^{29}Si NMR spectrum, δ, ppm: 2.29. Found, %: C 28.25, H 5.30; F 18.83, N 5.07; S 21.54. $C_7H_{16}F_3NO_2S_2Si$. Calculated, %: C 28.47, H 5.46, F 19.29, N 4.74; S 21.71.

Methylethyl-(*N*-trifluoromethanesulfonyl)sulfimide (IV). To a solution of 0.154 g of sulfide **I** in 3 ml of methanol a solution of 0.376 g of salt **II** in 4 ml of methanol was added dropwise during 15 min at room temperature, the mixture was stirred for 20 h, the solvent was removed, the residue thoroughly washed with ether, and dried over $MgSO_4$ to obtain 0.19 g (82%) of crude product **IV**, which was purified by column chromatography on silica gel (Merck) in the system hexane–ether from 20:1 to 1:1, ether–methanol from 20:1 to 1:4. IR spectrum, ν, cm^{-1}: 2886 (CH_2), 1335 (SO_2), 1218, 1182 (CF_3), 1141 (SO_2), 1010, 736 (S=N), 961 (NSO_2), 610. ^{1}H NMR spectrum, δ, ppm: 1.35 t (3H, CMe, *J* 7.4 Hz), 2.73 s (3H, SMe), 2.99 d.q (1H, SCH^{A}, *J* 13.2, 7.2 Hz), 3.05 d.q (1H, SCH^{B}, *J* 13.2, 7.2 Hz). ^{1}H NMR spectrum, DMSO-d_6, δ, ppm: 1.31 t (3H, CMe, *J* 7.3 Hz), 2.83 s (3H, SMe), 3.07 d.q

(1H, SCH^A, *J* 13.2, 7.2 Hz), 3.23 d.q (1H, SCH^B, *J* 13.2, 7.3 Hz). ^{13}C NMR spectrum, δ, ppm: 6.88 (C*C*H$_3$), 33.15 (SMe), 44.24 (S*C*C), 120.05 q (CF$_3$, J_{CF} 322.8 Hz). ^{19}F NMR spectrum, δ, ppm: –77.53. Found, %: C 21.25, H 3.50, N 6.63, F 25.53, S 29.12. $C_4H_8F_3NO_2S_2$. Calculated, %: C 21.52, H 3.59, N 6.28, F 25.56, S 28.70.

4,4-Dimethyl-4-silathiane-1-(*N*-trifluoromethanesulfonyl)sulfimide (VII). To 0.1 g of compound **V** in 1.5 ml of MeOH a solution of 0.224 g of salt **II** in 3.5 ml of methanol was added dropwise during 30 min at room temperature, the mixture was stirred for 5 h, methanol was removed, the extract after water–ether treatment was dried over MgSO$_4$. After removal of solvent and drying in a vacuum 0.105 g (52%) of the crude product **VII** was obtained. The yield of pure product **VII** after washing with ether for removal of siloxanes was 40%. NMR spectra coincide with those of the authentic sample prepared under aprotic conditions [11].

Reaction of 4,4-dimethyl-4-silathiane (V) with *N*,*N*-dichlorotrifluoromethanesulfonamide. To a solution of 0.251 g of compound **V** in 5 ml of CCl$_4$ 0.432 g of *N*,*N*-dichlorotrifluoro-methanesulfonamide in 5 ml of CC1$_4$ was added dropwise during 30 min at room temperature, the reaction mixture was stirred for 15 min at 40°C and 1 h at room temperature, washed with water, dried over MgSO$_4$. After removal of solvent, 0.203 g of oil was obtained that contained, by the data of ^{1}H NMR spectroscopy, ~30% of the target product **VII**, as well as the products of its decomposition with the ring opening.

3,3-Dimethyl-3-silathiane-1-(*N*-trifluoromethanesulfonyl)sulfimide (X). To a mixture of 0.158 g of compound **VIII**, 0.0126 g of triethylbenzylammonium chloride, and freshly calcined zeolites in 2.5 ml of anhydrous CH$_2$Cl$_2$ at –5°C 0.266 g of salt **II** was added by portions during 30 min, the reaction mixture was stirred for 45 min, allowed to warm to room temperature, kept for another 3 h, washed with cold water (2× 5 ml), dried over MgSO$_4$. After removal of solvent, 0.251 g (79%) of the product was obtained that was purified by column chromatography on silica gel (Merck) in the system hexane–ether from 8:1 to 1:7, ether. White crystalline compound was obtained with mp 149–151°C. IR spectrum, ν, cm^{-1}: 2900 (CH$_2$), 1420 (SiCH$_2$), 1290 (SO$_2$), 1230 (SiMe), 1190, 1140, (CF$_3$), 1100 (SO$_2$), 960, 780 (S=N), 920 (NSO$_2$), 800, 580. ^{1}H NMR spectrum, δ, ppm: 0.27 s (3H, SiMe), 0.31 s (3H, SiMe), 0.73 d.d.d (1H, H$_{4ax}$ ^2J 15.2, $^3J_{4ax5ax}$ 12.5, $^3J_{4ax5eq}$ 4.6 Hz), 0.86 d.d.d.t (1H, H$_{4eq}$ $^3J_{4eq5ax}$ 6.2, $^3J_{4eq5eq}$ 3.4, $^4J_{4eq6eq}$ = $^4J_{4eq2eq}$ 1.0 Hz), 1.94 d.d.d.d.d (1H, H$^5_{ax}$, $^2J_{5ax5eq}$ 16.0, $^3J_{5ax6ax}$ 12.0, $^3J_{5ax6eq}$ 6.6 Hz), 2.48 d.d.d.d.d (1H, H$_{5eq}$), 2.58 d (1H, H$_{2ax}$, $^2J_{2ax2eq}$ 13.1 Hz), 2.63 d.d.d (1H, H$^2_{eq}$, $^4J_{2eq6eq}$ 2.5, $^4J_{2eq4eq}$ 1.0 Hz), 3.02 d.d.d (1H, H$_{6ax}$, $^2J_{6ax6eq}$ 13.1, $^3J_{6ax5ax}$ 12.0, $^3J_{6ax5eq}$ 2.3 Hz), 3.24 d.d.d.d.d (1H, H$^6_{eq}$, $^2J_{6ax6eq}$ 13.1, $^3J_{6eq5ax}$ 6.6, $^3J_{6eq5eq}$ 2.4 Hz). ^{13}C NMR spectrum, δ, ppm: –3.45, –1.93 (SiMe), 11.15 (Si*C*C), 18.58 (C*C*C), 36.21 (SiCS), 50.71 (C*C*S), 120.16 q (CF$_3$, $^1J_{CF}$ 322.8 Hz). ^{19}F NMR spectrum, δ, ppm: –78.22. ^{29}Si NMR spectrum, δ, ppm: 0.24. Found, %: C 28.86; H 4.48; F 18.96; N 4.62; S 21.78. $C_7H_{14}F_3NO_2S_2Si$. Calculated, %: C 28.67; H 4.78; F 19.45; N 4.78; S 21.84.

Reaction of 3,3-dimethyl-3-silathiane (VIII) with salt II in methanol. To a solution of 0.105 g of compound **VIII** in 2 ml of anhydrous methanol the solution of 0.229 g of salt **II** in 3 ml of methanol was added dropwise during 25 min at –5°C, and the reaction mixture was stirred for 1 h at –5°C. Analysis by the ^{1}H and ^{29}Si NMR spectroscopy showed the absence in the reaction mixture of cyclic compounds **VIII** or **X**. After column chromatography on silica gel (eluents hexane, hexane–ether 8:1–1:5, ether–methanol 20:1–1:1) the fraction was obtained, which contained, according to NMR, methoxysilane **XI** and silanol **XII** in comparable amounts.

$Me_2Si(OMe)(CH_2)_3S(CH_3)=NSO_2CF_3$ (XI). ^{1}H NMR spectrum, δ, ppm: 0.10 s (6H, SiMe$_2$), 0.70 m (2H, SiCH$_2$), 1.65 m (2H, CCH$_2$C), 2.80 s (3H, SMe), 2.98 m (2H, SCH$_2$), 3.34 s (3H, MeO). ^{13}C NMR spectrum, δ, ppm: –2.80 (SiMe), 14.61 (Si*C*C), 17.13 (C*C*C), 34.08 (SMe), 50.54 (OMe), 53.67 (C*C*S). ^{19}F NMR spectrum, δ, ppm: –77.89. ^{29}Si NMR spectrum, δ, ppm: 19.99.

$Me_2Si(OH)(CH_2)_3S(CH_3)=NSO_2CF_3$ (XII). ^{1}H NMR spectrum, δ, ppm: 0.14 s (6H, SiMe$_2$), 0.78 m (2H, SiCH$_2$), 1.89 m (2H, CCH$_2$C), 2.79 s (3H, SMe), 3.15 m (2H, SCH$_2$), 4.62 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –77.79. ^{29}Si NMR spectrum, δ, ppm: 16.22. ^{29}Si NMR spectrum of the product of alkaline hydrolysis of sulfimide **X** in water–organic media contains the only signal at 8 ppm, which is indicative of formation of disiloxane **$CF_3SO_2N=S(Me)\cdot(CH_2)_3SiMe_2]_2O$ (XIII)**. ^{1}H NMR spectrum, DMSO-d_6, δ, ppm: 0.06 s (6H, SiMe$_2$), 0.60 m (1H, SiCH^A), 0.69 m (1H, SiCH^B), 1.65 m (1H, CCH^{A}C), 1.73 m (1H, CCH^{B}C), 2.85 s (3H, SMe), 3.17 t (2H, SCH$_2$, *J*

7.2 Hz). ^{13}C NMR spectrum, DMSO-d_6, δ, ppm: 0.25 ($SiMe_2$), 16.40 (Si*C*C), 16.79 (C*C*C), 33.79 (SiMe), 52.10 (C*C*S). ^{19}F NMR spectrum, $CDCl_3$, δ, ppm: –77.82. ^{29}Si NMR spectrum, DMSO-d_6, δ, ppm: 8.03.

3,3-Dimethyl-1-thia-3-silacyclopentane-1-(*N*-trifluoromethanesulfonyl)sulfimide (XV). To a mixture of 0.104 g of compound **XIV**, 0.008 g of triethylbenzylammonium chloride, and freshly calcined zeolites in 4 ml of anhydrous CH_2Cl_2 at –7°C in an argon atmosphere 0.192 g of salt **II** was added by portions during 30 min, the reaction mixture was stirred for 45 min at this temperature and allowed to warm to 3°C without stirring for sedimentation of the precipitate. The content of the target product **XV** with respect to all solutes in the reaction mixture, according to the data of ^{1}H NMR, was 75%. ^{1}H NMR spectrum, δ, ppm: 0.26 s (3H, SiMe), 0.43 s (3H, SiMe), 1.22 d.d.d (1H, H^{4A}, ^2J 14.79, $^3J_{4A5A}$ 7.3, $^3J_{4A5B}$ 3.8 Hz), 1.53 d.d.d (1H, H^{4B}, $^3J_{4B5A}$ 10.7, $^3J_{4B5B}$ 7.87 Hz), 2.09 d (1H, H^{2A}, ^2J 15.0 Hz), 2.27 d.d (1H, H^{2B}, $^4J_{2B5B}$ 2.4 Hz), 2.92 d.d.d (1H, H^{5A}, ^2J 13.8 Hz), 3.44 d.d.d.d (1H, H^{5B}, $^4J_{5B2B}$ 2.4 Hz). ^{13}C NMR spectrum, δ, ppm: –2.43, –0.99 (SiMe), 8.31 (Si*C*C), 33.13 (SiCS), 49.70 (C*C*S). ^{19}F NMR spectrum, δ, ppm: –78.56. ^{29}Si NMR spectrum, δ, ppm: 25.34.

After treatment of the reaction mixture with water, separation of organic layer, drying and removal of solvent, 0.218 g of the residue was obtained (yield of the crude product 95%), which was purified by column chromatography on silica gel, eluents hexane, hexane–ether (8:1–1:5), ether–methanol (20:1–1:1) to give disiloxane **$[CF_3SO_2N{=}S(Me)(CH_2)_2SiMe_2]_2O$ (XVII).** ^{1}H NMR spectrum, δ, ppm: 0.18 s (6H, $SiMe_2$), 1.01 d.d.d (1H, $SiCH^A$, ^2J 14.8, ^3J 13.4 and 4.6 Hz), 1.14 d.d.d (1H, $SiCH^B$), 2.79 s (3H, SCH_3), 3.07 d.d.d (1H, SCH^A, ^2J 14.0 Hz). ^{13}C NMR spectrum, δ, ppm: 0.50 ($SiMe_2$), 11.20 ($SiCH_2$), 33.01 (SCH_3), 47.01 (CH_2S), 120.30 q (CF_3, $^1J_{CF}$ 320.0 Hz). ^{19}F NMR spectrum, δ, ppm: –77.87, –77.93. ^{29}Si NMR spectrum, δ, ppm: 8.14, 8.35.

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REFERENCES

1. Gilchrist, T.L. and Moody, C.J., *Chem. Rev.*, 1977, vol. 77, no. 3, p. 409.
2. Kucsmann, A. and Kapovits, I., *Phosphorus Sulfur*, 1977, vol. 3, no. 1, p. 9.
3. Koval', I.V., *Russ. Chem. Rev. Engl. Transl.*, 1990, vol. 59, no. 9, p. 819.
4. Koval, I.V., *Sulf. Rep*., 1993, vol. 14, p. 149.
5. Taylor, P.C., *Sulf. Rep*., 1999, vol. 21, p. 241.
6. Roesky, H.W. and Holtschneider, G., *Z. Anorg. Allg. Chem*., 1970, vol. 378, no. 2, p. 168.
7. Behrend, E. and Haas, A., *J. Fluor. Chem*., 1974, vol. 4, no. 1, p. 83.
8. Kondratenko, N.V., Popov, V.I., Timofeeva, G.N., Ignat'ev, N.V., and Yagupol'skii, L.M., *Zh. Org. Khim*., 1984, vol., 20, no. 12, p. 2599.
9. Kondratenko, N.V., Gavrilova, R.Yu., and Yagupol'skii, L.M., *Zh. Org. Khim*., 1988, vol. 24, no. 3, p. 456.
10. Gavrilova, R.Yu., Kondratenko, N.V., Popov, V.I., and Yagupol'skii, L.M., *Zh. Org. Khim*., 1989, vol. 25, no. 5, p. 1118.
11. Suslova, E.N. and Shainyan, B.A., *Russ. J. Gen. Chem*., 2009, vol. 79, no. 5, p. 1045.
12. Rousseau, G. and Blanco, L., *Tetrahedron*, 2006, vol. 62, no. 34, p. 7951.
13. Kirpichenko, S.V., Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *Sulfur Lett*., 1999, vol. 22, no. 6, p. 245.
14. Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *Russ. J. Gen. Chem*., 2005, vol. 75, no. 8, p. 1234.
15. Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *J. Organometal. Chem*., 2003, vol. 677, nos. 1–2, p. 73.
16. Suslova, E.N., Kirpichenko, S.V., Albanov, A.I., and Shainyan B.A., *J. Chem. Soc. Perkin Trans. 1*, 2000, no. 18, p. 3140.
17. Voronkov, M.G., Mileshkevich, V.P., and Yuzhelevskii, Yu.A., *Siloksanovaya svaz'* (The Siloxane Bond), Movosibirsk: Nauka, 1976.
18. Ruff, F. and Kucsman, A., *J. Chem. Soc. Perkin Trans. 2,* 1975, no. 6, p. 509.
19. Yamamoto, T., Yoshida, D., Hojyo, J., and Terauchi, H., *Bull. Chem. Soc. Japan*, 1984, vol. 57, no. 11, p. 3341.
20. Tarasenko, N.A., Volkova, V.V., Zaikin, V.G., Mikaya, A.I., Tishenkov, A.A., Avakyan, V.G., and Gusel'nikov, L.E., *J. Organometal. Chem*., 1985, vol. 288, no. 1, p. 27.
21. Nazaretyan, V.P., Radchenko, O.A., and Yagupol'skii, L.M., *Zh. Org. Khim*., 1974, vol. 10, no. 11, p. 2460.
22. Cooper, G.D., *J. Am. Chem. Soc*., 1954, vol. 76, no. 14, p. 3713.
23. Kirpichenko, S.V., Suslova, E.N., Tolstikova, L.L., Albanov, A.I., and Shainyan, B.A., *Russ. J. Gen. Chem*., 1997, vol. 67, no. 9, p. 1449.
24. Borisenko, K., Samdal, S., Suslova, E.N., Sipachev, V.A., Shishkov, I.F., and Vilkov, L.V., *Acta Chem. Scand*., 1988, vol. 52, no. 8, p. 975.