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Synthesis and relative stability of five- and six-membered *S*-functional derivatives of 1,3-thiasilacycloalkanes

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Abstract

Oxidation, imidation, and *S*-methylation reactions of five- and six-membered 1,3-thiasilacycloalkanes have been examined under various conditions. The *S*-functional derivatives of 1,3-thiasilacycloalkanes undergo solvolytic Si–C(S) bond cleavage in protic media. The ease of the ring opening depends on the *S*-functionality and on the ring size.

Keywords: Thiasilacycloalkanes; *S*-Functionalization; Oxidation; Imidation; Methanolysis

1. Introduction

S-Functionalization of thiacycloalkanes by oxidation to sulfoxides or sulfones, or imidation to sulfimides, or *S*-alkylation leading to sulfonium salts generally presents no problem and is not complicated by side reactions of ring opening. Silicon-containing thiacycloalkanes with two heteroatoms separated by one or two methylene groups are also rather stable themselves [1–4]. Only in the case of 2-phenyl-3,3-dimethyl-1,3-silathiane the formation of the corresponding disiloxane is observed due to alkaline hydrolytic opening of the cycle (Scheme 1) [2].

Specific behavior of compound **1** is, apparently, due to stabilization of the intermediate α-carbanion by the phenyl group, which facilitates the Si–C_α bond rupture. This effect of an intermediate α-carbanion stabilization by *S*-functional group is responsible for the well-documented Si–C_α bond cleavage by the action of nucleophiles, in particular oxy-anions, on acyclic silicon-containing carbofunctional compounds having in the α-position RSO, RSO_2, RS=NR′, or R_2S^+ group [5–11].

Therefore, the preparation of *S*-functional derivatives of compounds of our continuing interest, 1,3-thiasilacycloalkanes, is a challenging problem. Earlier we have described the synthesis of some six-membered cyclic compounds of this type [4,12,13]. Continuating our studies on transformations of 1,3-thiasilacycloalkanes we report here the synthesis of new five- and six-membered *S*-functional derivatives of thiasilacycloalkanes. Subsequent transformations of these compounds proceeding with the ring opening have been studied and their relative solvolytic stability assessed.

2. Results and discussion

We have previously shown that 3,3-dimethyl-3-silathiane *S*-oxide (**4**) and 3,3-dimethyl-3-silathiane *S*,*S*-dioxide (**5**) are formed in high yield by oxidation of silathiane **3** with one or two equivalents of *m*-chloroperbenzoic acid (mCPBA) under aprotic conditions [4]. Both sulfoxide **4** and sulfone **5** are rather tolerant to hydrolysis. They endure work up with sodium bicarbonate and column chromatography on silica gel that considerably facilitates their isolation. Moreover, both are formed in high yield by oxidation with sodium periodate in aqueous methanol (Scheme 2).

The corresponding five-membered analogs turned out to be much less hydrolytically stable. Thus, oxidation of

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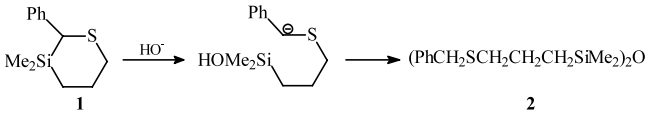
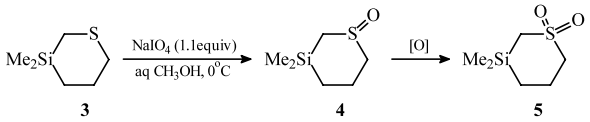


Scheme 1.

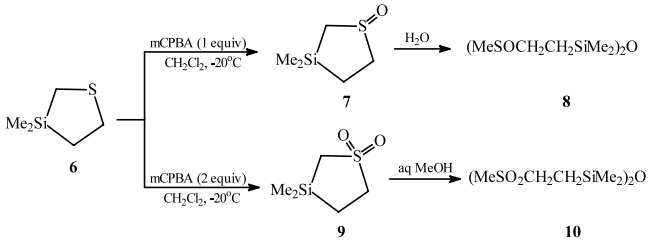


Scheme 2.

3,3-dimethyl-3-sila-1-thiacyclopentane (**6**) with one equivalent of mCPBA in CH_2Cl_2 at −20 °C proceeds with its complete conversion into sulfoxide **7**, as proved by ^{1}H-, *j*-modulated ^{13}C-, and ^{29}Si-NMR spectra of the crude product. Its structure was proven by the signals of diastereotopic protons of all three methylene groups and two signals of diastereotopic Me_2Si groups in the ^{1}H-NMR spectrum. However, we failed to isolate pure sulfoxide **7** due to its low stability. Work up similar to that for sulfoxide **4** leads to decomposition and appearance of new signals of Me_2Si groups. An attempt to isolate product **7** by three- to fourfold freezing out mCPBA or column chromatography using protic or aprotic eluents also led to complete decomposition of sulfoxide **7**. The only isolated product was disiloxane **8** formed by ring opening in **7** (Scheme 3).

Diastereotopic protons of the two methylene groups in **8** have virtually equal vicinal coupling constants (13.6 and 5.2 Hz), which testifies to the *s-trans* arrangement of the two heteroatoms in the S–C–C–Si fragment.

In order to avoid a necessary separation of the target sulfoxide from the acid, we have studied oxidation of sulfide **6** with mild neutral oxidizing agent $NaIO_4$ under various conditions. Under standard conditions of Scheme 2, sulfide **6** is completely converted into sulfoxide **7**, but the latter suffers ring opening to afford disiloxane **8**, and only 10% of sulfoxide **7** was detected in the crude product by ^{1}H- and ^{13}C-NMR. Oxidation in the two-phase system (CH_2Cl_2/H_2O, 2:1) in the presence of 10 mol% of benzyltriethylammonium chloride or 20 mol% of 15-crown-5 allowed us to avoid an undesirable reaction of the ring opening, and disiloxane **8** was not detected in the reaction mixture. However, because of low conversion (not exceeding 50%), similar solubility of



Scheme 3.

sulfide **6** and sulfoxide **7** even in nonpolar solvents, and chromatographic lability of sulfoxide **7**, we failed to isolate it in pure form. The fact that five-membered sulfoxide **7** is less stable than its six-membered analog **4** was proven directly by ^{1}H-NMR monitoring of their solutions in $CDCl_3$. The former was more than half-decomposed after 24 h, whereas the latter remained intact after 2 weeks.

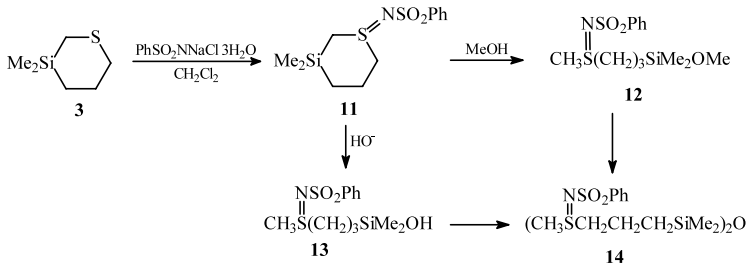
Oxidation of sulfide **6** with twofold excess of mCPBA gives the corresponding sulfone **9** (Scheme 3). The latter is much more stable as compared to sulfoxide **7** and was obtained in high isolated yield. Yet, it is less stable than its six-membered analog **5**, since oxidation with two equivalents of $NaIO_4$ in methanol gives mainly disiloxane **8**. Sulfone **9** also decomposes during aqueous work up or column chromatography to afford disiloxane **10**. Only 10% of sulfone **9** remained in aqueous methanol after 1 day, whereas its six-membered analog **5** remained intact under these conditions after 4 days.

We have recently shown that acyclic organosilicon α-sulfimides, which are *N*-analogs of α-sulfoxides, are formed from the corresponding sulfides by the reaction with chloramine B trihydrate under phase-transfer conditions. For example, methyl-(trimethylsilyl)methyl sulfide (Me_3SiCH_2SMe) gives α-silylsulfimide ($Me_3SiCH_2S(=NSO_2Ph)Me$). When methanol is used as a solvent the latter suffers the Si–C_α bond cleavage to Me_3SiOMe and $Me_2S{=}NSO_2Ph$ [8].

Based on these results we have examined in more detail the reaction of imidation of cyclic sulfide **3** described in Ref. [13]. Cyclic sulfimide **11** is formed in good yield (74%) when the reaction is performed under aprotic conditions with the use of phase-transfer catalyst (Scheme 4).

Pure sulfimide **11** is relatively stable and can be stored without decomposition in the cold for several months. However, in solution of **11** in aqueous methanol ($MeOH:H_2O$, 6:1) the ring opening by the Si–C_α bond takes place. ^{1}H-NMR monitoring showed that half life period at room temperature under these conditions is 24 h, and after 2 days the compound completely decomposes to afford the corresponding methoxysilane **12** and disiloxane **14** in equimolar ratio. Though the signals of diastereotopic methylene protons in the two compounds overlap, the ^{1}H-NMR spectrum of the crude product shows the signals of MeOSi (δ 3.34), SMe (δ 2.60), and Me_2Si (δ 0.024) groups in the ratio of 1:1:2, which corresponds to methoxysilane **12**.

Sulfimide **11** is much more sensitive to solvolysis than its oxygen analog **4**, which remains unchanged in aqueous methanol during 4 days. After column chromatography it is completely converted into the mixture of silanol **13** and disiloxane **14** of the 2:1 ratio. Compounds **13** and **14** were identified by comparing their ^{1}H-NMR spectra to those of authentic samples. Silanol **13** obtained by alkaline hydrolysis of sulfimide



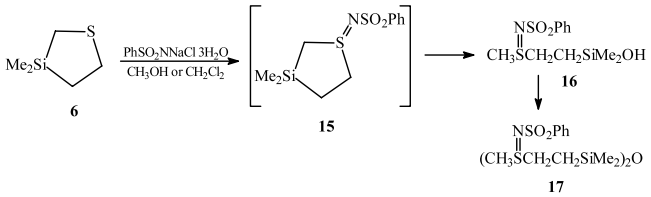
Scheme 4.

11 affords disiloxane **14** on long storage. Note that no hydrolysis of the S=N moiety was detected under the examined conditions.

Similar transformations take place when imidation of sulfide **3** is carried out directly in methanol. Column chromatography of the crude product affords the mixture of silanol **13** and disiloxane **14** in the ratio 1.5:2 in 72% total yield. Silanol **13** is apparently formed due to hydrolysis of methoxysilane **12** on silica gel. The final product isolated after treatment with sodium bicarbonate is pure disiloxane **14**. Earlier we erroneously assigned the structure of cyclic sulfimide **11** to this product [13]. The structure of **14** was proven by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopies. It should be noted that ^{1}H-NMR spectrum of disiloxane **14** shows two multiplets of $SiCH_2C$ and two singlets of SMe groups. Such complexity of the spectrum (the main reason of our erroneous assignment in Ref. [13]) is due to the fact that compound **14** has two chiral centers in the molecule and is a mixture of diastereomers.

Imidation of the five-membered sulfide **6** in methanol proceeds similarly (Scheme 5). Sulfide **6** is completely consumed after 1 h to afford two products, silanol **16** and disiloxane **17**, in 80% total yield. Their structure was confirmed by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra. The formation of silanol **16** is unequivocally proved by ^{29}Si chemical shift (δ_{Si} 12.0) characteristic of this class of organosilicon compounds. The ratio of **16**:**17** changes from 1.5:1 to 1:2 after removal of the solvent, and the subsequent column chromatography affords only disiloxane **17**. A more rapid conversion of silanol **16** to the corresponding disiloxane **17** as compared to silanol **13** to disiloxane **14** conversion is indicative of its lower stability. Treatment with sodium bicarbonate completely converts silanol **16** into disiloxane **17**.

As follows from the ^{1}H-NMR spectrum, disiloxane **17** is a mixture of two diastereomers. In ^{1}H-NMR spectrum

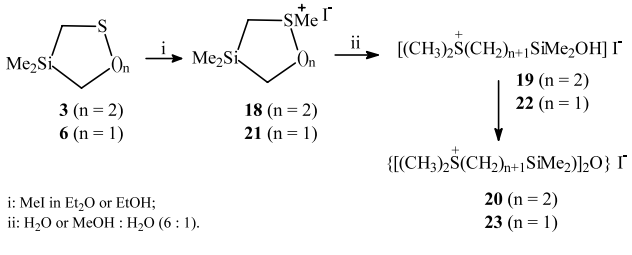


Scheme 5.

it results in doubled splitting for each of diastereotopic protons of the two methylene groups as compared to an ordinary ABMN spin system (see Section 3). As in the case of disiloxane **8**, similar coupling of the diastereotopic protons of both methylene groups in **17** with significantly different constants (14 and 4 Hz) is indicative of stable *s-trans* arrangement of the S–C–C–Si fragment. The ^{29}Si-NMR spectrum also shows two close signals.

Attempting to obtain five-membered cyclic sulfimide **15**, we carried out the imidation in methylene chloride. However, like in methanol and in contrast to Scheme 4, silanol **16** and disiloxane **17** remain to be the major products, and no traces of cyclic sulfimide were detected in the reaction mixture. Imidation in aprotic medium differs from the one in methanol only in that it affords sulfoxide **7** as a by-product. Sulfoxide **7** (contaminated with ring-opening products) was isolated by extraction and proven by coincidence of its ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra with those for the product of oxidation of sulfide **6** (Scheme 3). From the two possible routes of sulfoxide **7** formation, namely the hydrolysis of cyclic sulfimide or oxidation of the starting sulfide **6** by chloramine B, the latter path seems more plausible since even in methanol the ring opening of cyclic sulfimide proceeds with retention of the sulfimide moiety (Scheme 5).

Finally, we have studied hydrolytic ring opening in sulfonium salts **18** and **21** (Scheme 6). Compounds **18** and **21** were prepared by treatment of sulfides **3** and **6**, respectively, with methyl iodide in dry ethanol or ether.[1] The compounds were fairly stable under dry conditions.



Scheme 6.

[1] Salt **21** was prepared by us earlier [3] but no spectroscopic information was given.

When treated with aqueous methanol (MeOH:H_2O, 6:1) salt **18** suffers ring opening via splitting of the Si–C_α bond and gives silanol **19** and disiloxane **20** (75% conversion after 1 h, 100% after 5 h) in ~4:1 ratio. After 22 h exposure in aqueous methanol the ratio of **19**:**20** is inverted and consists 1:3, which indicates the following sequence of transformations shown in Scheme 6.

Under the same conditions salt **21** is completely ceased after only 1 h to afford disiloxane **23** as the main product. It suggests that, as with the aforesaid *S*-functional derivatives of thiasilacycloalkanes, the five-membered salt **21** is less stable than the six-membered salt **18**. The same is true for the relative stability of the silanols **19** and **22** derived from **18** and **21**. No silanol **22** was detected 5 h after treatment of **21** with aqueous methanol, whereas a similar treatment of **18** results in silanol **19** predominating in the mixture with disiloxane **20**. Pure silanol **22** was obtained by 17 h hydrolysis of **21** with D_2O in an NMR tube and characterized by IR and ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopies. On standing during several days it is gradually converted into disiloxane **23**. Since the signals in ^{1}H- and ^{13}C-NMR spectra of silanol **19** and disiloxane **20** (as well as of silanol **22** and disiloxane **23**) almost coincide, the ratios of the products were determined from their ^{29}Si-NMR, which are clearly different. The structure of silanols **19** and **22** was also corroborated by the presence of OH band in the IR spectra.

The conclusion can be drawn that *S*-functional derivatives of 1,3-thiasilacycloalkanes suffer solvolytic cleavage of the Si–C_α bond, with the ease of the ring opening depending on the nature of the *S*-functionality and the size of the ring. The five-membered compounds are split more readily than their six-membered analogs due to higher ring constraints. Six-membered *S*-functional derivatives rank in the following order of their solvolytic stability in aqueous methanol: sulfonium salt < sulfimide < sulfoxide ≤ sulfone. Another sequence is fulfilled for the five-membered analogs: sulfimide < sulfoxide < salt < sulfone.

3. Experimental

Melting points were determined with a Boetius apparatus (VEB Analytik) and are uncorrected. Infrared spectra were obtained on a Specord 75 IR spectrophotometer in thin layer or in pellets with KBr and given as ν_{max} (cm^{-1}). ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded for $CDCl_3$ solutions on a Bruker DPX-400 spectrometer at 400, 100, and 80 MHz, respectively. Chemical shifts were determined relative to residual chloroform signal and are given in ppm with respect to Me_4Si. Thin layer chromatography was performed on silica gel plates (60 F-254) and visualized by iodine vapors. All reactions were carried out under argon with standard precautions taken to avoid moisture. Solvents were dried and purified according to standard procedures and stored over molecular sieves 4A. Merck Kieselgel 60 (35–70-mesh) was used for column chromatography and the eluents are given in parentheses. Structural assignments for all new compounds were supported by *j*-modulated ^{13}C-NMR spectra.

Thiasilacycloalkanes **3** and **6**, sulfoxide **4**, and sulfone **5** were prepared according to Refs. [4,14]. 3,3-Dimethyl-3-sila-1-thiacyclopentane (**6**). IR (neat): 2950–2890, 1250 (MeSi), 830 (C–S). ^{1}H-NMR: $\delta = 0.19$ (s, 6H, Me_2Si), 1.01 (t, $^3J = 7.14$ Hz, 2H, $SiCH_2C$), 1.72 (s, 2H, $SiCH_2S$), 2.79 (t, 2H, CCH_2S). ^{13}C-NMR: $\delta = -2.79$ (Me_2Si), 13.35 (Si*C*C), 16.43 (SiCS), 30.92 (C*C*S). ^{29}Si-NMR: $\delta = 24.71$.

3.1. Reaction of 3,3-dimethyl-3-sila-1-thiacyclohexane (3) with $NaIO_4$

To a solution of **3** (290 mg, 2.0 mmol) in MeOH (25 ml) was added $NaIO_4$ (450 mg, 2.1 mmol) in H_2O (6 ml) at −2 °C. The mixture was stirred for 1 h, warmed to room temperature (r.t.), filtered and concentrated under vacuum. The residue was extracted with CH_2Cl_2 (4 × 3 ml) and dried over $MgSO_4$. The solvent was removed and the crude product (270 mg, 84% yield) purified by column chromatography to give 3,3-dimethyl-3-sila-1-thiacyclohexane *S*-oxide (**4**) (140 mg, 44% yield) as fine white crystals; m.p. 54–55 °C. ^{1}H- and ^{13}C-NMR data are consistent with those reported in Ref. [4]. With two equivalents of $NaIO_4$ 3,3-dimethyl-3-sila-1-thiacyclohexane *S*,*S*-dioxide (**5**) was obtained in 52% yield; m.p. 63–64 °C. Its ^{1}H-NMR spectrum coincides to that in Ref. [4]. ^{13}C-NMR: $\delta = -3.03$ (Me_2Si), 11.42 (Si*C*C), 19.51 (C*C*C), 44.37 (SiCS), 54.50 (S*C*C). ^{29}Si-NMR: $\delta = 1.17$.

3.2. Reaction of 3,3-dimethyl-3-sila-1-thiacyclopentane (6) with mCPBA

To a solution of **6** (300 mg, 2.3 mmol) in CH_2Cl_2 (3.5 ml) was added a solution of mCPBA (85%, 460 mg, 2.3 mmol) in CH_2Cl_2 (8 ml) at −20 °C. The mixture was stirred for 40 min and allowed to warm to 10 °C. At this stage the mixture consisted mainly (>90%) of sulfoxide **7** and only traces of sulfide **6**. 3,3-Dimethyl-3-sila-1-thiacyclopentane *S*-oxide (**7**), ^{1}H-NMR: $\delta = 0.18$ (s, 3H, $SiCH_3$), 0.36 (s, 3H, $SiCH_3$), 1.04 (ddd, $^2J_{4a4b} = 14.7$, $^3J_{4a5a} = 7.1$, $^3J_{4a5b} = 3.6$ Hz, 1H, $SiCH_2C$), 1.37 (ddd, $^3J_{4b5a} = 11.3$, $^3J_{4b5b} = 7.6$ Hz, 1H, $SiCH_2C$), 1.78 (dd, $^2J_{2a2b} = 14.7$, $^4J_{2a5a} = 0.8$ Hz, 1H, $SiCH_2S$), 2.07 (dd, $^4J_{2b5b} = 2.6$ Hz, 1H, $SiCH_2S$), 2.45 (dddd, $^2J_{5a5b} = 13.7$ Hz, 1H, CCH_2S), 3.17 (dddd, 1H, CCH_2S). ^{13}C-NMR: $\delta = -1.59$ (MeSi), 0.01 (MeSi), 7.95 (Si*C*C), 38.96 (SiCS), 51.39 (C*C*S). ^{29}Si-NMR: $\delta = 21.96$. Removal

of mCPBA by threefold freezing-out the above mixture in the presence of molecular sieves 4A gave crude product (130 mg) containing 65% of **7**. It was dissolved in CH_2Cl_2 and washed with cold 5% solution of $NaHCO_3$. Organic layer was separated, aqueous phase extracted twice with CH_2Cl_2, and combined organic phases dried over $MgSO_4$. The solvent was removed, the residue chromatographed (ethyl acetate:MeOH, 7:3 to 3:7) to give 1,1,3,3-tetramethyl-1,3-[bis(methylsulfinyl)ethyl]disiloxane (**8**) (50 mg, 14% yield) as colorless oil. IR (KBr): 2950, 1250 (MeSi), 1025 (SO), 1045 (SiOSi). ^{1}H-NMR: $\delta = 0.14$ (s, 12H, Me_2Si), 0.86 (ddd, $^2J = 15.2$, $^3J = 13.6$, 5.2 Hz, 2H, H_A in $SiCH_2$), 0.99 (ddd, $^2J = 15.2$, $^3J = 13.6$, 5.2 Hz, 2H, H_B in $SiCH_2$), 2.55 (s, 6H, CH_3SO), 2.62 (ddd, $^2J = 13.6$ Hz, 2H, H_A in CH_2SO), 2.67 (ddd, 2H, H_B in CH_2SO). Small splittings were observed for the upfield H_A signal of the SCH_2 group (1.3 Hz) and for the CH_3SO group (1.0 Hz) due to nonequivalence of some chemical shifts in the two diastereomers of **8** possessing two chiral sulfur atoms. ^{13}C-NMR: $\delta = 0.36$ (MeSi); 10.18 ($SiCH_2$); 37.70 (SMe); 49.18 (SCH_2). ^{29}Si-NMR: $\delta = 8.22$. Anal. Calc. for $C_{10}H_{26}S_2Si_2O_3$: C, 38.22; H, 8.28; S, 20.38; Si, 17.83. Found: C, 37.90; H, 8.24; S, 20.20; Si, 17.87%.

3.3. Reaction of 3,3-dimethyl-3-sila-1-thiacyclopentane (*6*) with $NaIO_4$

The reaction of **6** (340 mg, 2.6 mmol) with $NaIO_4$ (580 mg, 2.7 mmol) was carried out and treated similar to that in Section 3.1. The crude product (260 mg, 70%) was purified by column chromatography to give **8** (150 mg, 37% isolated yield).

3.4. 3,3-Dimethyl-3-sila-1-thiacyclopentane S,S-dioxide (*9*)

A solution of mCPBA (80%, 1.0 g, 5.8 mmol) in CH_2Cl_2 (10 ml) was added to a solution of **6** (380 mg, 2.9 mmol) in CH_2Cl_2 (10 ml) at -20 °C and stirred for 2 h at -15 °C. mCPBA was separated by twofold freezing-out in the presence of powdered molecular sieves 4A. The solvent was removed, the crude solid product (340 mg) washed with hexane (12 ml), and dried under vacuum. Sulfone **9** (300 mg, 86% yield) was obtained as white crystals; m.p. 95–96 °C. IR (KBr): 2955, 1290 and 1140 (SO_2), 1255 (MeSi), 860, 820. ^{1}H-NMR: $\delta = 0.37$ (s, 6H, Me_2Si), 1.23 (t, $^3J = 10.0$ Hz, 2H, $SiCH_2C$), 2.44 (s, 2H, $SiCH_2S$), 3.10 (t, 2H, CCH_2S). ^{13}C-NMR: $\delta = 1.82$ (MeSi), 8.57 (Si*C*C), 39.42 (SiCS), 52.03 (C*C*S). ^{29}Si-NMR: $\delta = 12.73$. Anal. Calc. for $C_5H_{12}SiSO_2$: C, 36.56; H, 7.34; S, 19.52; Si, 17.08. Found: C, 36.81; H, 7.22; S, 19.19; Si, 17.02%.

3.5. 1,1,3,3-Tetramethyl-1,3-bis[2-(methylsulfonyl)ethyl]disiloxane (*10*)

3,3-Dimethyl-3-sila-1-thiacyclopentane *S*,*S*-dioxide (**9**) was dissolved in MeOH:H_2O (6:1). After 24 h the solvent was removed and the product dried under vacuum. IR (neat): 2950, 1280 and 1130 (SO_2), 1250 (MeSi), 1060 (SiOSi). ^{1}H-NMR: $\delta = 0.055$ (s, 6H, Me_2Si), 0.92 (m, 2H, $SiCH_2$), 2.81 (s, 3H, MeS), 2.89 (m, 2H, SCH_2). ^{29}Si-NMR: $\delta = 7.92$.

3.6. 3-(Benzenesulfonylimino)-1,1-dimethyl-1,3-silathiane (*11*)

To a mixture of sulfide **3** (350 mg, 2.4 mol%), tetraethylbenzylammonium chloride (28 mg, 5 mol%) and molecular sieves 4A (770 mg) in CH_2Cl_2 (6 ml), chloramine B trihydrate (700 mg, 2.6 mmol) was added by portions for 30 min at -5 °C. The mixture was stirred for 40 min, then warmed to 15 °C. Liquid part was decanted and solvent removed under vacuum. The residue (550 mg) was thrice washed with ether and dried under vacuum to give **11** (530 mg, 74% yield) as white crystals; m.p. 105–107 °C. IR (KBr): 2850–3070 (CH), 1630 (Ph), 1250 (MeSi), 1290, 1130, 1150 (SO_2), 970, 760 (SN), 845, 695 (CS-cycle). ^{1}H-NMR: $\delta = 0.17$ (s, 3H, MeSi), 0.22 (s, 3H, MeSi), 0.62 (ddd, $^2J = 15.0$, $^3J =$ 12.7, 4.6 Hz, 1H, $SiCH_2C$), 0.78 (ddd, $^3J = 5.9$, 3.3 Hz, 1H, $SiCH_2C$), 1.81 (ddddd, $^2J = 15.0$, 1H, H_5, CCH_2C), 2.36 (m, 1H, CCH_2C), 2.40 (dd, $^2J = 13.1$, $^4J_{2,6} = 1.5$ Hz, 1H, $SiCH_2S$), 2.45 (d, 1H, $SiCH_2S$), 2.85 (ddd, $^2J =$ 13.0, $^3J = 12.4$, 2.2 Hz, 1H, CCH_2S), 3.04 (m, $^3J_{6,5} = 6.3$ Hz, 1H, CCH_2S), 7.41 (3H, m, $H_{m,p}$), 7.86 (2H, m, H_o). ^{13}C-NMR: $\delta = -3.62$ (MeSi), -1.91 (MeSi), 11.36 (Si*C*C), 18.63 (C*C*C), 36.17 (SiCS), 50.52 (C*C*S), 126.07 (C_o), 128.56 (C_m), 131.04 (C_p), 144.74 (C_i). ^{29}Si-NMR: $\delta = -0.14$. Anal. Calc. for $C_{12}H_{19}NS_2SiO_2$: C, 47.84; H, 6.31; N, 4.65; S, 21.26; Si, 9.30. Found: C, 47.78; H, 6.52; N, 4.78; S, 21.04; Si, 9.41%.

3.7. Alkaline hydrolysis of sulfimide *11* to silanol *13*

To a solution of sulfimide **11** (130 mg, 0.4 mmol) in acetone (2 ml), KOH (70 mg, 1.3 mmol) in H_2O (2 ml) was added and stirred for 15 min at r.t. Then saturated aqueous solution of NH_4Cl was added, organic layer separated, water layer extracted with CH_2Cl_2, combined organic phase dried over $MgSO_4$ and evaporated in vacuum. The residue was washed with ether and dried under vacuum to give **13** (110 mg, 80%) as white crystals; m.p. 80–82 °C. IR (KBr): 3320 (OH), 3060 (Ph), 1250 (MeSi), 1290 and 1140 (SO_2), 920 and 740 (SN). ^{1}H-NMR (acetone-d_6): $\delta = 0.03$ (s, 6H, Me_2Si), 0.57 (m, 2H, $SiCH_2$), 1.68 (m, 2H, CCH_2C), 2.66 (s, 3H, SMe), 3.00 (m, 2H, CH_2S), 4.36 (s, 1H, OH), 7.49–7.83 (m, 5H, Ph). ^{13}C-NMR: $\delta = -0.35$ (MeSi), -0.21

(MeSi), 16.39 ($SiCH_2$), 17.28 (C*C*C), 34.06 (SMe), 53.50 (*C*H_2S), 126.29 (C_o), 128.83 (C_m), 131.47 (C_p), 144.16 (C_1). ^{29}Si-NMR: $\delta = 15.45$. Anal. Calc. for $C_{12}H_{21}NS_2SiO_3$: C, 45.14; H, 6.58; N, 4.38; S, 20.06; Si, 8.78. Found: C, 45.45; H, 6.70; N, 4.39; S, 20.27; Si, 9.16%.

3.8. Imidation of **3** in methanol

Imidation of **3** (350 mg, 2.4 mmol) with chloramine B trihydrate (680 mg, 2.6 mmol) was performed as described in Ref. [8]. After 1 h the mixture consisted of only decomposition products of sulfimide **11**. The crude product (800 mg) was chromatographed (hexane:ethyl acetate, 9:1 to 1:1, methanol) to give a 1.5:1 mixture (520 mg, 72% total yield) of silanol **13** and disiloxane **14**. Treatment of this mixture with 5% aqueous sodium bicarbonate completely converted silanol **13** to disiloxane **14** obtained as white crystals; m.p. 66–68 °C. IR (KBr): 3050, 1560 (Ph), 1280 and 1135 (SO_2), 1240 (Me_2Si), 1060 (SiOSi), 930 and 740 (S=N). ^{1}H-NMR: $\delta = -0.05$ (s, 12H, Me_2Si), 0.42 (m, 2H, H_A in $SiCH_2$), 0.52 (m, 2H, H_B in $SiCH_2$), 1.56 (m, 4H, CCH_2C), 2.54 (s, 3H, SMe), 2.55 (s, 3H, SMe), 2.89 (m, 4H, CH_2S), 7.37 (m, 6H, $H_{m,p}$), 7.80 (m, 4H, H_o). ^{13}C-NMR: $\delta = 0.38$ (MeSi), 17.22 ($SiCH_2$), 17.49 (C*C*C), 34.32 (SMe), 53.37 (CH_2S), 126.35 (C_o), 128.96 (C_m), 131.53 (C_p), 144.57 (C_1). ^{29}Si-NMR: $\delta = 7.30$. Anal. Calc. for $C_{22}H_{40}N_2O_5S_4Si_2$: C, 46.01; H, 6.41; N, 4.58; S, 20.94; Si, 8.79. Found: C, 46.42; H, 6.49; N, 4.51; S, 20.65; Si, 9.05%.

3.9. Imidation of **6** in methanol

In a similar way, **6** (190 mg, 1.4 mmol) reacted with chloramine B trihydrate (410 mg, 1.5 mmol) with 100% conversion after 1 h into the mixture of silanol **16** and disiloxane **17** in the ratio 1.5:1. After filtering on Celite 521 the ratio changed to 1:2 (total yield: 400 mg, 80%). Column chromatography or washing with 10% sodium bicarbonate gave pure disiloxane **17** as white glassy solid. IR (KBr): 3060 and 1580 (Ph), 1290 and 1130 (SO_2), 1250 (MeSi), 1060 (SiOSi), 940 and 750 (SN). ^{1}H-NMR: $\delta = -0.06$ (s, 12H, Me_2Si), 0.718 (ddd, $^2J = 13.8$ Hz, $^3J = 13.8$, 4.3 Hz, 1H, H_A in $SiCH_2$), 0.723 (ddd, $^3J = 13.8$, 4.2 Hz, 1H, H_B in $SiCH_2$), 0.86 (ddd, $^2J = 13.8$ Hz, $^3J = 13.8$, 4.3 Hz, 1H, H_A in $SiCH_2'$), 0.88 (ddd, $^3J = 13.7$, 4.3 Hz, 1H, H_B in $SiCH_2'$), 2.61 (s, 3H, MeS), 2.63 (s, 3H, MeS), 2.85 (ddd, $^2J = 13.2$ Hz, $^3J = 10.2$, 3.9 Hz, 1H, H_A in SCH_2), 2.88 (ddd, $^3J = 10.1$, 4.1 Hz, 1H, H_B in SCH_2), 3.02 (ddd, $^2J = 13.3$ Hz, $^3J = 13.3$, 4.4 Hz, 2H, $H_A + H_B$ in SCH_2'), 7.44 (m, 6H, $H_{m,p}$), 7.82 (m, 4H, H_o). ^{13}C-NMR: $\delta = -0.33$ (MeSi), 10.20 (Si*C*C), 32.22 (SMe), 45.44 (C*C*S), 125.53 (C_o), 128.23 (C_m), 130.86 (C_p), 143.66 (C_1). ^{29}Si-NMR: $\delta = 8.23$, 8.29. Anal. Calc. for $C_{20}H_{36}N_2O_5S_4Si_2$: C, 44.59; H, 6.08; N, 4.73; S, 21.62; Si, 9.46. Found: C, 44.49; H, 5.91; N, 4.58; S, 21.99; Si, 9.39%.

3.10. Imidation of **6** in CH_2Cl_2

Under the conditions of synthesis of sulfimide **11** the reaction of sulfide **6** (400 mg, 3.0 mmol) with chloramine B trihydrate (810 mg, 3.0 mmol) after 1 h gave a mixture of silanol **16** (48%), disiloxane **17** (24%), and sulfoxide **7** (28%). The latter was separated by extraction with ether as an oil. Its ^{13}C-NMR spectrum completely coincided with that from oxidation of sulfide **6** with mCPBA. At the same time, the SiCS and S*C*C signals in the six-membered compounds **4** and **11** differ by 4–6 ppm. Therefore, we can rule out the formation of cyclic sulfimide **15** in the reaction of **6** with chloramine B. The residue after extraction consisted of silanol **16** and disiloxane **17** in the ratio 1:2 contaminated with benzenesulfonamide. Column chromatography (hexane:ether, 7:1; ether:methanol, from 20:1 to 1:1) afforded pure disiloxane **17** (110 mg, 24%).

3.11. 1,3,3-Trimethyl-1,3-thiasilinan-1-ium iodide (**18**)

A mixture of sulfide **3** (610 mg, 4.2 mmol) and CH_3I (1.78 g, 12.5 mmol) in EtOH (3 ml) was kept for 5 days at r.t., the solvent removed, and the residue (1.17 g) crystallized from CH_2Cl_2/ether (1:3) to give **17** (1.14 g, 95%) as white crystals; m.p. 84–85 °C. IR (KBr): 2920, 1250 (MeSi), 1090 (SMe). ^{1}H-NMR: $\delta = 0.34$ (s, 6H, Me_2Si), 0.95 (d, $^2J = 15.2$ Hz, 1H, H_A in $SiCH_2C$), 1.12 (ddd, $^3J = 14.3$, 4.8 Hz, 1H, H_B in $SiCH_2C$), 2.03 (ddd, $^2J = 14.3$ Hz, 1H, H_A in CCH_2C), 2.55 (m, $^3J = 4.8$ Hz, 1H, H_B in CCH_2C), 3.02 (d, $^2J = 12.5$ Hz, 1H, H_A in $SiCH_2S$), 3.44 (s, 3H, SMe), 3.50 (d, 1H, H_B in $SiCH_2S$), 3.82 (d, $^2J = 13.1$ Hz, 1H, H_A in CCH_2S), 3.97 (t, $^3J =$ 14 Hz, 1H, H_B in CCH_2S). ^{13}C-NMR: $\delta = -2.5$ (MeSi), 10.92 (Si*C*C), 20.68 (C*C*C), 24.55 (SiCS), 29.92 (SMe), 41.70 (C*C*S). ^{29}Si-NMR: $\delta = -2.21$. Anal. Calc. for $C_7H_{17}ISSi$: I, 44.09; S, 11.11. Found: I, 44.36; S, 11.47%.

3.12. 1,3,3-Trimethyl-1,3-thiasilolan-1-ium iodide (**21**)

In a similar way from **6** (230 mg, 1.7 mmol) and CH_3I (710 mg, 5.0 mmol), **21** (470 mg, 96%) was obtained as white crystals; m.p. 160–161 °C (lit.: 159–160 °C [3]). IR (KBr): 2940, 1240 (MeSi), 1080 (SMe). ^{1}H-NMR: $\delta =$ 0.52 (s, 3H, MeSi), 0.45 (s, 3H, MeSi), 1.38 (ddd, $^2J =$ 15.2 Hz, $^3J = 10.1$, 8.3 Hz, 1H, H_A in $SiCH_2C$), 1.49 (ddd, $^3J = 7.2$ Hz, $^3J = 4.8$ Hz, 1H, H_B in $SiCH_2C$), 2.74 (dd, $^2J = 14.8$ Hz, $^4J = 1.2$ Hz, 1H, H_A in $SiCH_2S$), 3.05 (d, 1H, H_B in $SiCH_2S$), 3.16 (s, 3H, SMe), 4.07 (ddd, $^2J = 13.9$ Hz, 1H, H_A in CCH_2S), 4.14 (m, 1H, H_B in CCH_2S). ^{13}C-NMR: $\delta = -1.60$ (MeSi), -0.47 (MeSi), 10.67 (Si*C*C), 24.80 (SiCS), 25.51 (SMe), 43.98 (C*C*S). ^{29}Si-NMR: $\delta = 30.27$.

3.13. Methanolysis of salt **18**

120 mg (0.42 mmol) of salt **18** was dissolved in 2.4 ml of aqueous methanol (MeOH:H_2O, 6:1). The reaction leading to silanol **19** and disiloxane **20** was monitored at intervals by removing the solvent, drying the residue, and taking its NMR spectra. Pure disiloxane **20** was obtained by reprecipitation from acetone into ether (110 mg, 89%).

3.13.1. Silanol **19**

IR (KBr, vaseline oil): 3400 (OH), 1250 (MeSi), 1080 (Me_2S). ^{1}H-NMR (acetone-d_6): $\delta = 0.12$ (s, 6H, Me_2Si), 0.80 (m, 2H, $SiCH_2$), 2.01 (m, 2H, CCH_2C), 3.31 (s, 6H, Me_2S), 3.79 (m, 2H, SCH_2). ^{13}C-NMR (acetone-d_6): $\delta = -0.06$ (MeSi), 17.22 (Si*C*C), 19.14 (C*C*C), 25.21 (Me_2S), 46.06 (C*C*S). ^{29}Si-NMR (acetone-d_6): $\delta = 12.49$.

3.13.2. Disiloxane **20**

Light-yellow crystals; m.p. 141–143 °C. IR (KBr): 1250 (MeSi), 1090 (MeS), 1020 (SiOSi). ^{1}H-NMR (D_2O): $\delta = 0.076$ (s, 6H, Me_2Si), 0.69 (m, 2H, $SiCH_2$), 1.79 (m, 2H, CCH_2C), 2.85 (s, 3H, MeS), 3.28 (m, 2H, SCH_2). ^{13}C-NMR (acetone-d_6): $\delta = -0.04$ (MeSi), 17.23 (Si*C*C), 19.28 (C*C*C), 25.42 (Me_2S), 46.08 (C*C*S). ^{29}Si-NMR (acetone-d_6): $\delta = 7.69$. Anal. Calc. for $C_{14}H_{36}I_2OS_2Si_2$: I, 42.76; S, 10.77. Found: I, 42.05; S, 10.69%.

3.14. Hydrolysis of salt **21**

3.14.1. Silanol **22**

Hydrolysis of salt **21** in D_2O for 17 h at r.t. gave silanol **22**. IR (after careful drying in KBr and in vaseline oil): 3410 (OH), 1250 (MeSi), 1050 (MeS). ^{1}H-NMR (D_2O): $\delta = 0.14$ (s, 6H, Me_2Si), 1.06 (m, 2H, $SiCH_2$), 2.76 (s, 6H, Me_2S), 3.30 (m, 2H, SCH_2). ^{13}C-NMR (D_2O): $\delta = -1.91$ (MeSi), 11.08 (Si*C*C), 23.41 (Me_2S), 39.70 (C*C*S). ^{29}Si-NMR: $\delta = 16.00$ (in D_2O); 12.49 (in acetone-d_6).

3.15. Methanolysis of salt **21**

Methanolysis of 180 mg (0.66 mmol) of salt **21** was performed and monitored similar to that in Section 3.13. Pure disiloxane **23** was obtained by reprecipitation from acetone into ether (140 mg, 74%) as yellowish crystals; m.p. 131–134 °C. IR (KBr): 1260 (MeSi), 1050 (MeS), 1020 (SiOSi). ^{1}H-NMR (D_2O): $\delta = 0.16$ (s, 6H, Me_2Si), 1.06 (m, 2H, $SiCH_2C$), 2.77 (s, 6H, Me_2S), 3.29 (m, 2H, CCH_2S). ^{13}C-NMR (D_2O): $\delta = -0.30$ (MeSi), 11.81 ($SiCH_2$), 23.79 (Me_2S), 40.23 (S*C*C). ^{29}Si-NMR (D_2O): $\delta = 9.22$. Anal. Calc. for $C_{12}H_{32}I_2OS_2Si_2$: I, 44.88; S, 11.31. Found: I, 44.84; S, 11.70%.

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