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Synthesis of acyclic α- and β-silyl sulfimides

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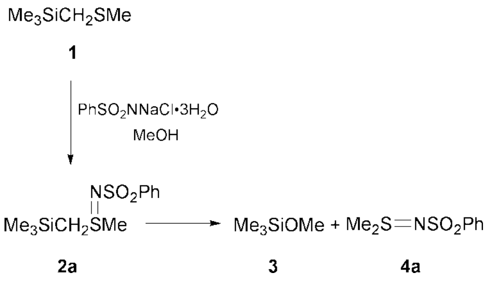
Conversion of acyclic α- and β-silyl sulfides by their treatment with sodium salts of *N*-chlorosulfonamides into the corresponding previously unknown sulfimides is described. The process is accompanied by a competing reaction resulting in the formation of α- or β-silyl sulfoxides. β-Silyl sulfimide (**9b**) undergoes thermolysis to generate trimethylvinylsilane.

Recently we have described the preparation of the first acyclic organosilicon sulfimide having the S=N moiety in the γ-position to the silicon atom. However, attempts to obtain the corresponding α-silyl sulfimide by the reaction of trimethylsilylmethyl ethyl sulfide with chloramine B in methanol led only to the isolation of the silicon-free sulfimide.[1]

Now we report a detailed study of the reaction of α- and β-organosilicon sulfides with chloramines as well as some chemical properties of the new α- and β-silyl sulfimides.

Results and discussion

Treatment of trimethylsilylmethyl methyl sulfide **1** with chloramine B in methanol results in its complete disappearance and the formation of the expected α-silyl sulfimide **2a** (Scheme 1).



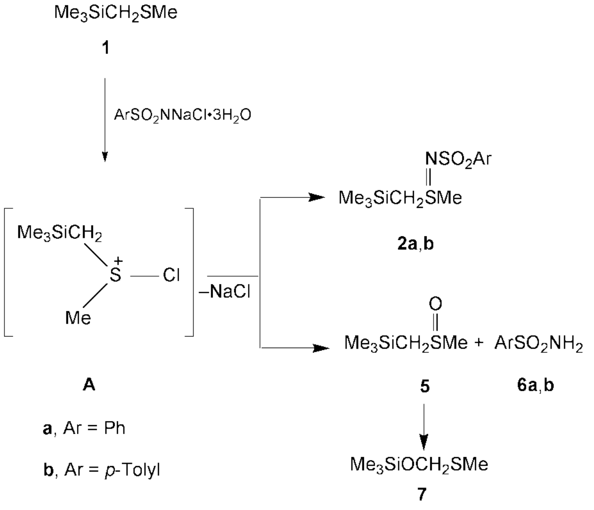
Scheme 1

Its structure was confirmed by comparison of the ^{1}H NMR spectrum of the reaction mixture with that of pure **2a** obtained as described below.

However, isolation of pure sulfimide **2a** was greatly hindered due to its solvolytic and hydrolytic lability. Thus, silica gel column chromatography of the crude product after removal of volatile components afforded sulfimide **4a** in 75% yield. Trimethylmethoxysilane **3** was proved by ^{29}Si NMR spectroscopy to be the sole organosilicon compound present after the total decomposition of sulfimide **2a**.

To avoid the cleavage of the Si–C bond of **2a** we used methylene chloride as a solvent in place of methanol. However, the reaction occurred with a low conversion (25%) of sulfide **1** owing to the poor solubility of chloramines in this solvent. Using benzyltriethylammonium chloride as a phase-transfer catalyst[2] facilitates the conversion of sulfide **1** which proceeds *via* two competing reactions (Scheme 2).

The ^{1}H NMR spectrum of the crude reaction mixture consists of two well-resolved sets of similar chemical shifts of protons of the Me_3Si and SMe groups as well as two pairs of signals of the diastereotopic protons of the Si–CH_2S units. One set of peaks is associated with sulfimide **2a** (see Experimental section), while the singlet at δ 0.12 (Me_3Si), doublets at δ 2.13 and 2.30 (diastereotopic protons of the $SiCH_2$, $^2J_{AB}$ 13.6 Hz) and the singlet at δ 2.50 (SMe) can be assigned to sulfoxide **5**.



Scheme 2

As in the case of dialkyl sulfides,[3] the above reactions involve the same intermediate chlorosulfonium ion **A** which is attacked by either N- or O-nucleophiles to give α-silyl sulfimides **2a**,**b** or α-silyl sulfoxide **5**, respectively. Thus, the ratio of **2a** : **5** was estimated to be 3 : 1 from the peak areas of the corresponding Me_3Si and S–Me protons. In addition, arenesulfonamides **6a**,**b** are formed along with sulfoxide **5**.

α-Silyl alkyl sulfoxides were found to be thermally unstable due to a facile sila-Pummerer rearrangement which can occur even below room temperature.[4,5] For this reason we failed to isolate pure sulfoxide **5** and observed its conversion into the *O*-trimethylsilyl hemithioacetal **7** when the reaction mixture was allowed to stand at room temperature. ^{1}H NMR monitoring revealed that the signals relating to the sulfoxide **5** disappear, while a singlet appears at δ 4.45 ppm which was assigned to the Si–O–CH_2–S unit in **7**.[6]

We believe that the formation of sulfoxide **5** can be explained by the presence of water of hydration or traces of moisture in the system. Indeed, when sulfide **1** reacts with chloramine B under water free conditions (in the presence of 4 Å molecular sieves) sulfimide **2a** is obtained as the sole product some starting compound **1** being recovered. ^{1}H NMR monitoring

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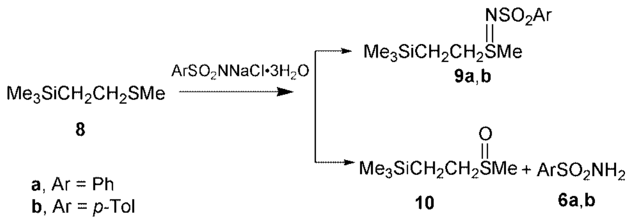
showed that sulfimide **2a** was relatively long-lived (*ca.* 4 days) in $CDCl_3$ solution under rigorous exclusion of air and moisture. Due to decomposition and the loss of the product during the work-up procedure, compound **2a** was isolated analytically pure only in low yield (about 10%).

Remarkably, the acyclic and cyclic six-membered α-silyl sulfoxide and α-silyl sulfimide show very different stability: the latter are solvolytically and thermally more stable than their open-chain analogs.[1,7]

β-Silyl sulfide **8** also reacts readily with chloramine B (or T) in methanol or methylene chloride to afford a mixture of β-silyl sulfimide **9a** and β-silyl sulfoxide **10** in a ~2 : 1 ratio, respectively (Scheme 3).

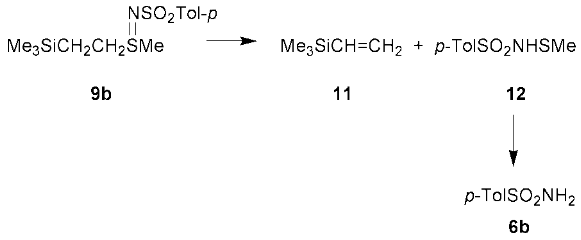


Scheme 3

The compounds were separated by column chromatography and appeared to be stable. In particular, they can be stored in a refrigerator for several months without detectable decomposition. Their structure was proved by the ABXX′ spin system shape of the CH_2CH_2 fragments.

It should be noted that a higher electron density at the sulfur atom in α-silyl sulfides as compared with β-silyl sulfides[8] favors their transformations so that the reaction in Scheme 2 is much more exothermic than the reaction outlined in Scheme 3. As noted previously, the increasing +*I*-effect of the S-substituents facilitates the imidation reaction of dialkyl sulfides.[9]

Like β-silyl sulfoxides,[10] β-silyl sulfimides undergo thermal decomposition to generate vinyl silanes (Scheme 4). Thus, heating of a DMSO solution of **9b** in an NMR tube at 110 °C for 10 min results in the appearance in the spectrum of a well-defined ABC spin system in the olefinic region at 5.6–6.3 ppm, as well as a new Me_3Si group at 0.06 ppm, all chemical shifts and couplings completely coinciding with those of an authentic sample of trimethylvinylsilane **11** [δ 0.02 (Me_3Si), 5.69 (H_A), 5.93 (H_B), 6.15 (H_C), *J* 4.0, 14.6, 20.3 Hz]. The presence of sulfonamide **6b** was proved by comparison of the spectrum of the thermolysis products with that of an authentic sample. *N*-(Methylthio)sulfonamide **12** formed as an intermediate could be detected by NMR (δ_{NH} 9.63 in DMSO-d_6) but was not isolated.



Scheme 4

Experimental

IR spectra were recorded on a Specord-IR-29 spectrophotometer in pellets with KBr. ^1H, ^{13}C, and ^{29}Si NMR spectra were measured on a Bruker DPX spectrometer operating at 400 MHz for protons, 100 MHz for carbon and 80 MHz for the silicon nucleus. *J* values are given in Hz. All spectra were obtained for solutions in $CDCl_3$, chemical shifts given in ppm are relative to tetramethylsilane as internal standard. Mps were determined with a Boetius apparatus (VEB Analytik) and are uncorrected. Thin layer chromatography was carried out on silica gel plates (60 F-254) using UV light (254 nm) as visualizing agent. Merck silica gel 60 (35–70 mesh) was used for column chromatography. Solvents used were freshly distilled from appropriate drying agents under an atmosphere of dry argon prior to use: diethyl ether and tetrahydrofuran (THF) (lithium aluminium hydride), methylene chloride, hexane and ethyl acetate (calcium hydride). Methanol was distilled from magnesium metal activated with iodine and stored over 4 Å molecular sieves. All reactions were carried out in flame-dried glassware under an argon atmosphere. Standard precautions to avoid moisture were taken.

2-(Trimethylsilyl)ethyl methyl sulfide 8

Obtained by methylation of 2-(trimethylsilyl)ethanethiol with methyl iodide in the presence of sodium hydride in THF by the known procedure.[11]

Reaction of trimethylsilylmethyl methyl sulfide 1 with chloramines

(a) Chloramine B trihydrate (0.60 g, 2.24 mmol) in methanol (6 ml) was added to a solution of sulfide **1**[12] (0.30 g, 2.2 mmol) in methanol (4 ml) at −5 °C. The resulting mixture was stirred for 1 h at this temperature and then allowed to stand overnight at room temperature. Volatile products were collected under reduced pressure and distilled to give *trimethylmethoxysilane* **3** (0.12 g, 51%) contaminated with methanol. Compound **3** was identified by gas chromatography (10% Lukopren G-1000 on 45–60 mesh Chromaton N-AW-HMDS) by comparison with an authentic sample and by its ^{29}Si NMR spectrum which is identical with that reported.[13] Chromatography of the remaining material on silica gel (hexane–ethyl acetate 9 : 1 to 0 : 1, MeOH) gave *N-(phenylsulfonyl)-S,S-dimethylsulfimide* **4a** (0.37 g, 75%) as white crystals, mp 129–130 °C,[14] δ_H 2.64 (6H, s, Me_2S), 7.43 (3H, m, $H_{m,p}$), 7.83 (2H, d, H_o).

(b) To a stirred solution of sulfide **1** (0.21 g, 1.6 mmol) and benzyltriethylammonium chloride (0.05 mol%, 0.02 g) in methylene chloride (5 ml) was slowly added solid chloramine B trihydrate (0.42 g, 1.6 mmol) in the presence of powdered 4 Å molecular sieves (0.50 g) at −5 °C. When the addition of chloramine was completed, the reaction mixture was stirred for 1 h at this temperature and was allowed to warm to room temperature. The NaCl formed was filtered and the solvent was removed on a rotary evaporator. The crude residue was dissolved in ether, and after filtration to remove insoluble material, the extract was concentrated under vacuum. This procedure was repeated 2–3 times and the remaining white solid was dried under high vacuum (1 mmHg) for 1–2 h to afford *N-(phenylsulfonyl)-S-methyl-S-(trimethylsilylmethyl)-sulfimide* **2a** (0.045 g, isolated yield 10%), mp 30–32 °C (Found: C, 45.02; H, 6.60; N, 4.72; S, 22.29; Si, 8.93. $C_{11}H_{19}NS_2SiO_2$ requires C, 45.67; H, 6.57; N, 4.84; S, 22.15; Si, 9.69%); ν_{max}/cm^{-1} 3080, 1620 (Ph), 1280, 1130 (SO_2), 940, 735 (S=N) and 830 (Si–C); δ_H 0.20 (9H, s, Me_3Si), 2.19 (1H, d, H_A in $SiCH_2$), 2.42 (1H, d, H_B in $SiCH_2$, $^2J_{AB}$ 13.6), 2.55 (3H, s, SMe), 7.39 (3H, m, $H_{m,p}$), 7.75 (2H, d, H_o); δ_{Si} 0.235.

The work-up was accompanied by decomposition of compound **2a** to give sulfimide **4a** (0.34 g, 53%), which was purified as described above.

N-(*p*-Tolylsulfonyl)-*S*-methyl-*S*-(trimethylsilylmethyl)sulfimide 2b

Prepared from sulfide **1** as above with chloramine B (procedure b). Compound **2b** (0.04 g, 6%) was obtained as a white solid, mp 66–67 °C (Found: C, 46.89; H, 7.11; N, 4.63; S, 21.35; Si, 8.88. $C_{12}H_{21}NS_2SiO_2$ requires C, 47.52; H, 6.93; N, 4.62; S, 21.12; Si, 9.24%); ν_{max}/cm^{-1} 3040, 1600 (Ar), 1280, 1130 (SO_2), 940, 730 (S=N), 840 (Si–C) and 805 (Ar); δ_H 0.20 (9H, s, Me_3Si), 2.18 (1H, d, H_A in $SiCH_2$), 2.40 (1H, d, H_B in $SiCH_2$, $^2J_{AB}$ 13.5), 2.42 (3H, s, CMe), 2.62 (3H, s, SMe), 7.28 (2H, d, H_m), 7.79 (2H, d, H_o, ^3J 8.4). δ_{Si} −0.506.

In addition, *N-(p-tolylsulfonyl)-S,S-dimethylsulfimide* (**4b**) was obtained as a decomposition product in 65% yield, mp 157–159 °C.[14]

Reactions of 2-(trimethylsilyl)ethyl methyl sulfide 8 with chloramines

Chloramine B trihydrate (0.80 g, 2.97 mmol) was added to a solution of compound **8** (0.44 g, 2.97 mmol) and benzyltriethylammonium chloride (0.05 mol%, 0.03 g) in 10.5 ml methylene chloride at −5 °C and the mixture was stirred for 2 h at this temperature. The solvent was removed under reduced pressure and the residue chromatographed on silica gel with a system of increasing polarity (hexane–ethyl acetate 9 : 1 to 0 : 1, MeOH). Two fractions were isolated, one containing *N-(phenylsulfonyl)-S-methyl-S-[2-(trimethylsilyl)ethyl]sulfimide* **9a** (0.53 g, 59%), and the other containing *methyl 2-(trimethylsilyl)ethyl sulfoxide* **10** (0.18 g, 36%).

A similar procedure with chloramine T gave *N-(p-tolylsulfonyl)-S-methyl-S-[2-(trimethylsilyl)ethyl]sulfimide* **9b** (0.33 g, 65%), and compound **10** (0.10 g, 33%).

Compound **9a**: R_f (ethyl acetate) 0.5. White crystals, mp 63–65 °C (Found: C, 46.89; H, 6.20; N, 4.34; S, 21.24; Si, 9.05. $C_{12}H_{21}NS_2SiO_2$ requires C, 47.52; H, 6.93; N, 4.62; S, 21.12; Si, 9.24%); ν_{max}/cm^{-1} 3070, 1630 (Ph), 1290, 1130 (SO_2), 970, 740 (S=N); δ_H 0.006 (9H, s, Me_3Si), 0.64, 0.84 (2H, m, $SiCH_2$, AB-part of the ABXX′ spin system, $^2J_{AB}$ 13.6, $^3J_{AX} = {}^3J_{BX'} = 4.2$, $^3J_{AX'} = {}^3J_{BX} = 14.1$), 2.53 (3H, s, SMe), 2.82 (2H, m, CH_2S, XX′-part of the ABXX′ spin system, $^2J_{XX'}$ 1.5), 7.45 (3H, m, $H_{m,p}$), 7.90 (2H, d, H_o); δ_C −2.07 (Me_3Si), 9.62 ($SiCH_2$), 32.98 (SMe), 47.23 (SCH_2), 126.73 (C_m), 128.56 (C_o), 131.14 (C_p), 144.47 (C_i); δ_{Si} 2.95.

Compound **9b**: R_f (ethyl acetate) 0.5. White crystals, mp 93–95 °C (Found: C, 49.28; H, 7.29; N, 4.45; S, 20.78; Si, 8.38. $C_{13}H_{23}NS_2SiO_2$ requires C, 49.21; H, 7.26; N, 4.42; S, 20.19; Si, 8.83%); ν_{max}/cm^{-1} 3020, 1600 (Ph), 1290, 1130 (SO_2), 970, 750 (S=N) and 805 (Ar); δ_H 0.006 (9H, s, Me_3Si), 0.67 and 0.85 (2H, m, $SiCH_2$, AB-part of the ABXX′ spin system, $^2J_{AB}$ 21.32, $^3J_{XX'}$ 4.49, $^3J_{AX'} = {}^3J_{BX} = 15.99$, $^3J_{AX} = {}^3J_{BX'} = 6.33$), 2.38 (3H, s, CMe), 2.56 (3H, s, SMe), 2.81 (2H, m, CH_2S, XX′-part of the ABXX′ spin system), 7.22 (2H, d, ^3J 8.06, H_m), 7.78 (2H, d, H_o).

Compound **10**: R_f 0.80. Yellow oil (Found: C, 43.60; H, 9.75; S, 19.88; Si 16.89. $C_6H_{16}SSiO$ requires C, 43.85; H, 9.81; S, 19.51; Si 17.09%); ν_{max}/cm^{-1} 1250 (Me_3Si), 1030 (S=O), 870, 840 (C-S); δ_H 0.08 (9H, s, Me_3Si), 0.81, 0.95 (2H, m, $SiCH_2$, AB-part of the ABXX′ spin system, $^2J_{AB}$ 18.01, $^2J_{XX'}$ 5.04, $^3J_{AX} = {}^3J_{BX'} = {}^3J_{AX'} = {}^3J_{BX} = 9.13$), 2.54 (3H, s, SMe), 2.65 (2H, m, SCH_2, XX′-part of the ABXX′ spin system); δ_C −1.91 (Me_3Si), 8.61 (Si*C*H_2), 37.36 (SMe), 49.83 (S*C*H_2); δ_{Si} 2.97.

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