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4,4-Dimethyl-3,4-dihydro-2*H*-1,4-thiasiline – the first cyclic organosilicon vinyl sulfide

Elena N. Suslova and Bagrat A. Shainyan*

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 41 9346; email: bagrat@irioch.irk.ru

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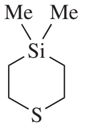
The Pummerer rearrangement of 4,4-dimethyl-1,4-thiasilinane 1-oxide affords 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline, the first cyclic organosilicon vinyl sulfide.

The literature data on the six-membered Si,S-cyclic compounds with 1,4-positioned heteroatoms and non-functionalized sulfur atom are very scarce. 4,4-Dimethyl-1,4-thiasilinane **1** was first prepared 30 years ago[1] and its synthesis was modified later on.[2] Compounds with the C=C double bond in the ring of type **2** were not known. The closest analogues are the commercially available 10,10-dimethyl-10*H*-phenothiasiline **3**[3] and dithienothiasiline **4** possessing hole conductivity.[4]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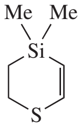
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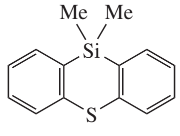
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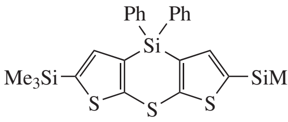
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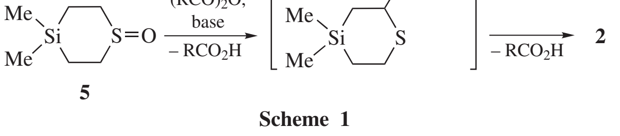
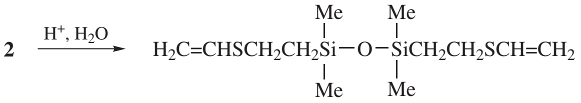
Silicon-free analogues of compound **2** (cyclic vinyl sulfides) are accessible by the Pummerer rearrangement of the corresponding saturated cyclic sulfoxides (see review[5]).

In the present work we report the synthesis of the first cyclic organosilicon vinyl sulfide, 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline **2** by the Pummerer rearrangement of 4,4-dimethyl-1,4-thiasilinane 1-oxide **5** (Scheme 1). This route represents a novel approach to organosilicon vinyl sulfides which so far were prepared by free-radical addition of thiols to ethynyl silanes.[6]


Scheme 1

As the standard electrophiles for the Pummerer rearrangement, benzoic, acetic and trifluoroacetic anhydrides as well as trimethylchlorosilane were examined. No reaction occurred with benzoic anhydride even after 14 h at 70 °C. On the contrary, with trimethylchlorosilane in dichloromethane without heating the substrate was completely decomposed after 15–30 min. With acetic anhydride, no reaction occurred in the absence of base, while in the presence of lutidine after 3 h at 120 °C only traces of product **2** were detected by ^{1}H NMR spectroscopy.

The best result was achieved with trifluoroacetic anhydride providing the target product **2** in 66% yield.[†] As a by-product, the product of its hydrolysis, *Si*,*Si'*-bis(2-vinylthioethyl)tetramethyldisiloxane **6** was formed in 21% yield (Scheme 2).



$$2 \xrightarrow{H^+,\ H_2O} \mathrm{H_2C{=}CHSCH_2CH_2}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}{-}\mathrm{O}{-}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{CH_2CH_2SCH{=}CH_2}$$

6

Scheme 2

This is indicative of a hydrolytic instability of compound **2**, as distinct from the linear analogues R_3Si–CH=CH–SR, which can be stored without decomposition for months.

Note that the isomer of compound **5** with 1,3-arrangement of heteroatoms in the ring, 3,3-dimethyl-1,3-thiasilinane 1-oxide, suffers thermal sila-Pummerer rearrangement with the ring expansion to give 7,7-dimethyl-1,3,7-oxathiasilepane.[7] At the same time, 1,4-thiasilinane 1-oxides, as we have shown earlier, are thermally stable.[8]

The composition of products **2** and **6** was proved by elemental analysis and their structure by IR and ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy.[‡]

In conclusion, the hitherto unknown approach to organosilicon vinyl sulfides is proposed based on the Pummerer rearrangement of the corresponding sulfoxides. The first cyclic organosilicon vinyl sulfide 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline is prepared from 4,4-dimethyl-1,4-thiasilinane 1-oxide, which in turn was obtained from commercially available dichlorodimethylsilane. Extension of this approach to other substrates is in progress.

[†] *Reaction of 4,4-dimethyl-1,4-thiasilinane 1-oxide* **5** *with trifluoroacetic anhydride*. To the solution of compound **5** (0.168 g, 1 mmol) and pyridine (0.164 g, 2.4 mmol) in abs. CH_2Cl_2 (25 ml) the solution of trifluoroacetic anhydride (0.25 g, 1.2 mmol) in CH_2Cl_2 (5 ml) was added dropwise in argon atmosphere within 15 min. The reaction mixture was stirred for 1.5 h at 0 °C, warmed to room temperature, the solvent was removed, the residue was twice extracted with pentane. After evacuation of pentane the product (0.14 g) contained, according to ^{1}H NMR, compounds **2** and **6** in the 3:1 ratio. The yield of crude **2** was 66%. Products **2** and **6** were purified by column chromatography on silica (Merck, Geduran) with eluent pentane–diethyl ether from 20:1 to 1:1.

[‡] ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400, 100 and 80 MHz, respectively). IR spectrum was recorded on a Bruker Vertex 70 spectrometer. The reactions were monitored by ^{1}H NMR and TLC on silica plates 60 F-254. The solvents were purified and dried by conventional methods and stored over molecular sieves 4A.

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*4,4-Dimethyl-3,4-dihydro-2*H*-1,4-thiasiline* **2**: ^{1}H NMR ($CDCl_3$) δ: 7.05 (d, 1H, SCH=, *J* 13.7 Hz), 5.74 (d, 1H, SiCH=, *J* 13.7 Hz), 3.02 (m, 2H, SCH_2), 1.09 (m, 2H, $SiCH_2$), 0.12 (s, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$) δ: 141.32 (SCH=), 121.02 (SiCH=), 26.50 (SCH_2), 12.95 ($SiCH_2$), 1.68 (SiMe). ^{29}Si NMR ($CDCl_3$) δ: –18.10. Found (%): C, 50.15; H, 8.49; S, 21.80; Si, 19.83. Calc. for $C_6H_{12}SSi$ (%): C, 49.95; H, 8.38; S, 22.22; Si, 19.45.

Si,Si'*-Bis(2-vinylthioethyl)tetramethyldisiloxane* **6**: IR (film, ν_{max}/cm^{-1}): 3093 (=CH_2), 2919 (CH_2), 1672 (C=C), 1254 ($SiMe_2$), 1059 (Si–O–Si), 839 (C–S). ^{1}H NMR ($CDCl_3$) δ: 6.38 (dd, 1H, SCH=, *J* 16.8 and 10.3 Hz), 5.21 (d, 1H, =CH_{cis}, *J* 10.3 Hz), 5.09 (d, 1H, =CH_{trans}, *J* 16.8 Hz), 2.76 (m, 2H, SCH_2), 0.96 (m, 2H, $SiCH_2$), 0.13 (s, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$) δ: 132.59 (SCH=), 110.53 (=CH_2), 26.38 (SCH_2), 18.34 ($SiCH_2$), 0.49 (SiMe). ^{29}Si NMR ($CDCl_3$) δ: 6.84. Found (%): C, 47.00; H, 8.59; S, 20.54; Si, 18.70. Calc. for $C_{12}H_{26}S_2Si_2O$ (%): C, 47.02; H, 8.55; S, 20.92; Si, 18.30.

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