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RESEARCH ARTICLE

CONFORMATIONAL BEHAVIOR OF 3,3-DIMETHYL-3-SILATHIANE 1-OXIDE AND ITS DIASTEREOMERIC 2-METHYL DERIVATIVES

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The conformational behavior of 3,3-dimethyl-3-silathiane 1-oxide **3** and its *trans*-**4** and *cis*-**4** 2-methyl derivatives has been studied by ^{1}H and ^{13}C NMR. The equatorial conformer **3**-eq for **3** and the diequatorial isomer *trans*-**4**-eq for *trans*-**4** predominate (>95%) in $CDCl_3$ solution. In contrast, the *cis*-**4**-ax conformer is the more preferred form of *cis*-**4**. The conformational free energy (ΔG^{o}) in the equilibrium *cis*-**4**-ax $\leftrightarrow$ *cis*-**4**-eq was determined to be about $+0.01$ and $+0.52$ kcal mol^{-1} at 26 and -120°C, respectively. The Gibbs free energy of activation ($\Delta G^{\ddagger}$) for the inversion *cis*-**4**-ax $\rightarrow$ *cis*-**4**-eq was estimated to be 8.1 kcal mol^{-1} at -100°C.

Keywords: Sulfur heterocycles; Organosilicon sulfoxides; Conformational analysis; NMR spectroscopy

INTRODUCTION

The chemistry of acyclic organosilicon sulfoxides especially those bearing both sulfur and silicon atoms on the same (α-silyl) or adjacent (β-silyl) carbon atom(s) continues to attract the considerable attention due to their synthetic potential [1, 2].

The usefulness of α-silyl sulfoxides for the preparation of various types of carbonyl compounds [1], vinyl sulfoxides [1] and heterocycles [1, 3, 4] has been demonstrated. β-Silyl sulfoxides can serve as a vinyl anion equivalent for the regiospecific synthesis of olefins and as suitable precursors for obtaining alkane-, arene- and 1-alkenesulfenyl chlorides [2]. Optically active 2-trimethylsilylethyl sulfoxides can be applied as the chiral silylated or non-silylated vinyl anion, vinyl dianion and ethynyl anion equivalents in asymmetric synthesis [2].

Organosilicon cyclic sulfoxides, in particular, six-membered cyclic sulfoxides, have not been properly studied and are of significant interest from both a mechanistic and synthetic point of view. A few examples of six-membered sulfoxides having an exocyclic triorganylsilyl group at the α-position have been reported [5–8]. Some of them appeared to be suitable substrates for stereoselective transformations. Thus, enantiomeric 2-trimethylsilylthiane 1-oxides have been successively employed for the preparation of stereoisomerically defined open-chain and cyclic alcohols [8].

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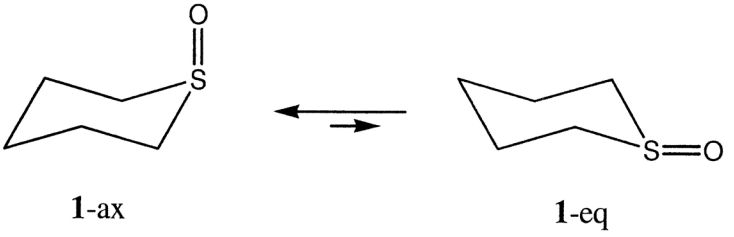
We previously prepared the first six-membered cyclic sulfoxide with two endocyclic heteroatoms, 3,3-dimethyl-3-silathiane 1-oxide [9]. It appeared to be sufficiently stable to allow a study of the kinetics of the sila-Pummerer rearrangement for the first time [10]. Our continuing study of the chemical behavior of silathiane 1-oxides prompted us to examine their conformational properties, which can affect their reactivity as well as the stereochemical outcome of some of their reactions.

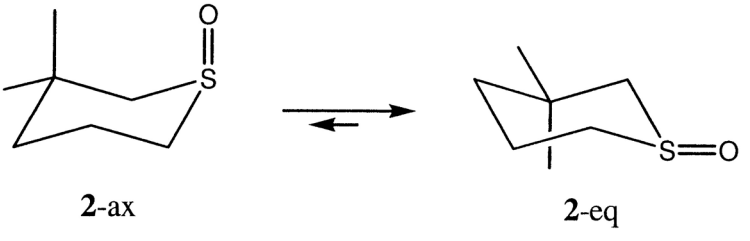
Conformations of related organic six-membered cyclic sulfoxides, thiane 1-oxide **1** and its derivatives, have been investigated by many experimental and computational methods [11–15]. Conformational equilibria of these compounds have been shown to be strongly affected by the presence of a second heteroatom in the ring or substituents at the C-ring atoms and by the nature of the solvent [11]. Thus, for thiane oxide **1** a slight axial preference of the sulfinyl oxygen ($\Delta G°_{-90°C} = +0.175$ kcal mol^{-1}, CH_2Cl_2) has been determined by low-temperature ^{1}H and ^{13}C NMR spectroscopy (Scheme 1) [16–20], but only axial chair form **1**-ax has been found in the gas phase by an electron diffraction study [21]. The higher stability of the axial conformer as compared with the equatorial one was explained by an attractive 1,3-*syn*-axial interaction between the oxygen and hydrogen atoms in the **1**-ax conformer and/or by a repulsion of the equatorial oxygen atom by its vicinal hydrogen atoms in **1**-eq [11].



1-ax **1**-eq

SCHEME 1

The introduction of two methyl groups at C-3 atom strongly disfavors the axial conformer due to van der Waals repulsion between SO-ax and the *syn*-axial methyl group, so that 3,3-dimethylthiane 1-oxide **2** exists in CD_2Cl_2 solution as the equatorial conformer **2**-eq exclusively (Scheme 2) [17, 19].

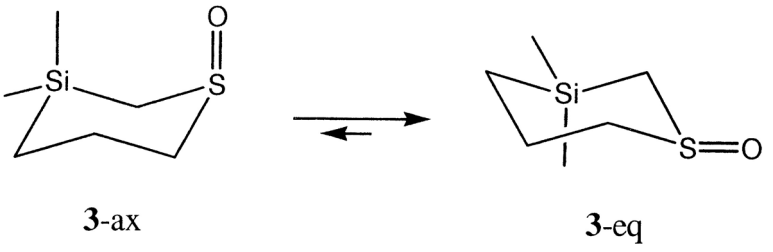


2-ax **2**-eq

SCHEME 2

In the preliminary report we assumed that in the sila-analog of compound **2**, 3,3-dimethyl-3-silathiane 1-oxide **3**, the longer endocyclic Si-C bond (1.904 Å) compared with the C−C bond (1.534 Å) should decrease the steric conflict of SO_{ax}/Me_{ax}. Based on ^{1}H NMR data at ambient temperature, both conformers **3**-ax and **3**-eq were suggested to be present in $CDCl_3$ solution, the latter being predominant (Scheme 3) [9].

We now report the first detailed study of the conformational behavior of sulfoxide **3** as well as *cis*-**4** and *trans*-**4** isomers of 2,3,3-trimethyl-3-silathiane 1-oxide **4** by ^{1}H and



3-ax **3**-eq

SCHEME 3

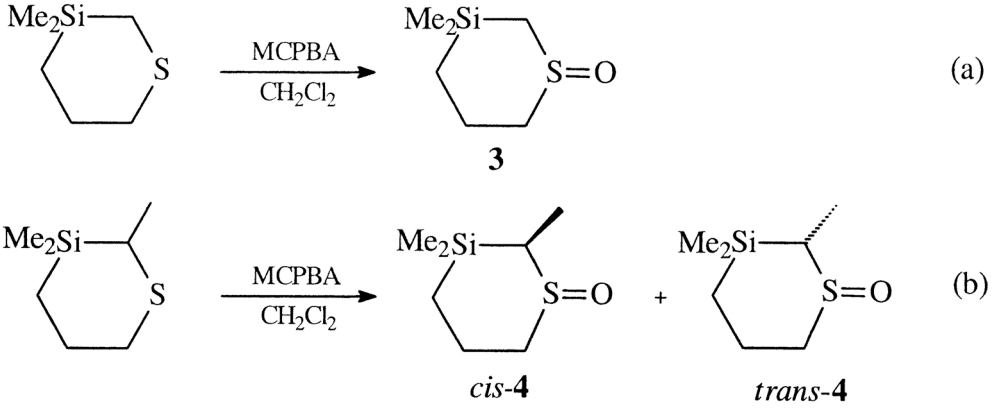
variable-temperature ^{13}C NMR spectroscopy. The aim was to gain insight into the conformational consequences of replacing a C-3 atom by a silicon atom in the thiane 1-oxide system.

RESULTS AND DISCUSSION

Compounds **3** and **4** were obtained by oxidation of the corresponding 3-silathianes as previously described (Scheme 4a,b) [9, 22]. A diastereomeric mixture (1:2) of 2-methyl substituted sulfoxides was separated by column chromatography on silica gel to give pure *cis*-**4** and *trans*-**4** isomers (Scheme 4b).

The major component was assigned to *trans*-**4** diastereomer since the ^{13}C NMR signals of its ring carbons were at lower field than those of the minor isomer (Table I). This assignment was based on the known stereochemical criteria for 2-alkyl substituted thiane 1-oxides [19, 23] and substantiated by detailed analysis of the conformational tendencies of compounds **4** (*vide infra*).

^{13}C and ^{1}H NMR data for sulfoxides **3** and *trans*-**4** (Tables I and II) demonstrate a definite similarity of most spectral parameters and, consequently, a conformational similarity of both



SCHEME 4

TABLE I Room temperature ^{13}C chemical shifts (δ in ppm) for **3**, *trans*-**4** and *cis*-**4** in $CDCl_3$.

Compound	*Me(Si)*	*Me(Si)*	*Me(C-2)*	*C-4*	*C-5*	*C-2*	*C-6*
3	−3.00	−1.60		12.15	17.02	43.05	54.28
trans-**4**	−6.22	−3.60	9.64	12.63	17.85	49.21	54.46
cis-**4**	−3.53	−3.19	6.86	10.81	15.03	41.42	47.59

TABLE II ^{1}H NMR data (δ in ppm; J in Hz) for compounds **3**, *trans*-**4** and *cis*-**4**[a] in $CDCl_3$ at room temperature.

	δ				$^nJ_{HH}$		
	3	***trans-4***	***cis-4***		***3***	***trans-4***	***cis-4***
MeSi	0.12	0.06	0.07				
	0.18	0.14	0.16				
H_{4ax}	0.56	0.57	0.56	$^2J_{4ax4eq}$	14.9	14.9	15.1
				$^3J_{4ax5ax}$	12.4	13.8	8.7
				$^3J_{4ax5eq}$	4.7	5.1	3.9
H_{4eq}	0.71	0.77	0.71	$^3J_{4eq5eq}$	6.1	4.7	9.8
MeC-2		1.40	1.31	$^2J_{MecH}$		7.2	7.4
H_{5ax}	1.73	1.73	1.76	$^2J_{5ax5eq}$	15.4	15.4	15.0
				$^3J_{5ax6ax}$	11.9	12.7	8.7
				$^3J_{5ax6eq}$	2.0	2.0	2.3
H_{2ax}	2.19	2.17	2.13	$^2J_{2ax2eq}$	12.9		
H_{5eq}	2.26	2.20	2.25	$^3J_{5eq6eq}$	7.0	6.2	9.7
				$^3J_{5eq6ax}$	2.2	2.0	2.0
H_{6ax}	2.55	2.56	2.78	$^2J_{6ax6eq}$	12.8	12.7	13.4
H_{2eq}	2.57			$^4J_{2eq4eq}$	1.1		
				$^4J_{2eq6eq}$	3.0		1.4
H_{6eq}	3.04	3.18	2.46	$^4J_{4eq6eq}$	1.1	1.3	

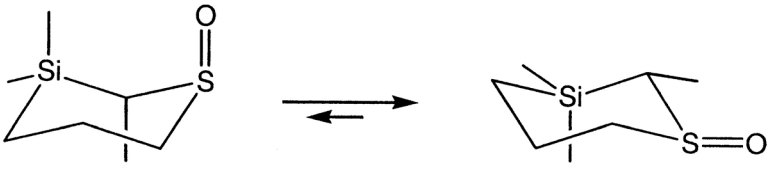
[a]Terms eq and ax for "mobile" compound *cis*-**4** refer to the protons predominantly equatorial and axial, respectively.

compounds. For example, the ^{13}C chemical shifts of the ring carbons C-4, C-5 and C-6 of **3** are almost identical to those of *trans*-**4** (Table I).

Related vicinal coupling constants $^3J_{HH}$ are also nearly the same (Table II), indicating that both compounds exist in the chair form with a very high preference for one of two possible orientations of the S=O group.

Compared with the *cis*-**4** isomer, sulfoxides **3** and *trans*-**4** differ by (a) the lesser shielding of their C-6 carbon; (b) the larger difference between the chemical shifts of the C-6 geminal protons and their lower field centerpoint; and (c) the smaller stereospecific coupling constants $^2J_{6ax6eq}$. According to known criteria [17], these data provide strong support for the equatorial preference of the sulfinyl oxygen in compounds **3** and *trans*-**4** and, consequently, for a very high shift of their conformational equilibria to the equatorial conformer **3**-eq and diequatorial isomer *trans*-**4**-eq, respectively, as shown in Schemes 3 and 5.

The ^{1}H NMR spectrum of *trans*-**4** does not exhibit the long-range "W" coupling constants $^4J_{2eq4eq}$ and $^4J_{2eq6eq}$, which are inherent for **3** (Table II). This also confirms that the proton at C-2 in *trans*-**4** is predominantly axial and as such incapable of W-coupling across the ring.



trans-**4**-ax *trans*-**4**-eq

SCHEME 5

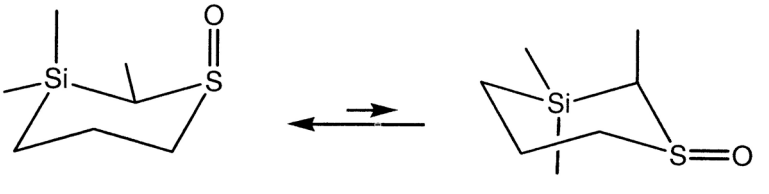
Variable-temperature ^{13}C NMR experiments indicate the lack of a dynamic behavior of the sulfoxides **3** and *trans*-**4** and thereby prove an essentially total predominance (>95%) of the **3**-eq and *trans*-**4**-eq conformers in the equilibria depicted in Schemes 3 and 5. Indeed, the number, position and shape of their ^{13}C NMR signals remain unchanged as the temperature decreases from 26 to −100°C, indicating no detectable presence of the second conformer.

To the contrary, the vicinal coupling constants in the ^{1}H NMR spectrum of *cis*-**4** isomer (Table II) are consistent with a fast ring inversion (on the NMR time scale) at ambient temperature, resulting in an average of the spectral parameters of the two conformations shown in Scheme 6. This is also true for the four-bond coupling ($^{4}J = 1.4$ Hz) between the proton at C-2 and the high-field proton at C-6 ($\delta = 2.46$ ppm).

First-order analysis of the splitting patterns shows that the average values of the vicinal *trans* coupling constants imply roughly equal populations of the conformers *cis*-**4**-ax and *cis*-**4**-eq at ambient temperature. Assuming that the coupling constants $^{3}J_{axax}$ and $^{3}J_{eqeq}$ are nearly the same as those in **3**-eq and *trans*-**4**-eq, we can estimate a ratio of *cis*-**4**-ax to *cis*-**4**-eq as 0.52:0.48. A similar ratio (0.53:0.47) can be calculated assuming the identity of $^{4}J_{2eq6eq}$ for *cis*-**4**-eq and **3**-eq (3.0 Hz) and the lack of the related W-type four-bond coupling for *cis*-**4**-ax. These ratios indicate a very small preference for the axial conformer of *cis*-**4** ($\Delta G^{o} = +0.01$ kcal mol^{-1}) at room temperature.

Analysis of the variable-temperature ^{13}C NMR spectra shows a drastic increase in the population of *cis*-**4**-ax with lowering temperature. As the temperature decreases, the ^{13}C signals for *cis*-**4** gradually broaden and shift to higher field (except for C-5). At −120°C, splitting is observed for all signals that results in two distinct sets of major and minor signals (Table III). Taking into account general shielding trends on going from the equatorial to the axial conformer [18, 19], we assigned the larger high-field signals to *cis*-**4**-ax.

By integration of the C-6 signal at δ 44.30 (major) and 47.35 (minor) the *cis*-**4**-ax to *cis*-**4**-eq ratio was found to be 5:1, which corresponds to a conformational free-energy difference $\Delta G^{o}_{-120°C}$ of +0.52 kcal mol^{-1}. The observed temperature dependence of the conformer populations implies that the *cis*-**4**-ax conformer is highly preferred at low temperature for enthalpic reasons, whereas at ambient temperature the entropic contribution to the ΔG^{o} favors the *cis*-**4**-eq conformation.



cis-**4**-ax *cis*-**4**-eq

SCHEME 6

TABLE III Variable-temperature ^{13}C chemical shifts (δ in ppm) for *cis*-**4** in CD_2Cl_2-$CDCl_3$-CCl_4 (4:2:1).

Compound	*T* (°C)	*Me_2Si*	*Me(C-2)*	*C-4*	*C-5*	*C-2*	*C-6*
cis-**4**	26	−4.00, −3.72	6.27	10.34	14.91	41.24	47.44
cis-**4**	−80	−4.20, −4.46	3.96	8.21	15.75	40.27	45.52
cis-**4**-ax	−120	−4.29, −5.06	1.97	6.46	17.10	40.32	44.30
cis-**4**-eq	−120	−3.62, −6.55	10.70	11.35	13.60	38.04	47.35

Based on the splitting and intensity ratio at −120°C for the C-6 signals, and on their coalescence temperature $T_c = -100$°C, the Gibbs free-energies of activation $\Delta G^{\ddagger}_{-100°C}$ for the inversion *cis*-**4**-ax → *cis*-**4**-eq and for the reverse process, *cis*-**4**-eq → *cis*-**4**-ax, were estimated to be 8.1 and 7.5 kcal mol^{-1}, respectively. These values are about half of that reported for the ring inversion of thiane 1-oxide **1** (14.2 kcal mol^{-1}) [16]. The lower activation barrier for *cis*-**4** as compared with that for **1** can be explained by an elongation of two endocyclic bonds and some ring flattening at a silicon that is characteristic of silacyclohexane derivatives [24–26].

From the above data we can conclude the following. Even though a Si−C bond is considerably longer than a C−C bond, a significant repulsion between the axial oxygen and *syn*-axial methyl group provides for the equatorial orientation of the S=O group in 3,3-dimethyl-3-silathiane 1-oxide (**3**) as well as in its carbon analog, 3,3-dimethylthiane 1-oxide (**2**). This unfavorable steric interaction, together with the tendency of a methyl group in thiane derivatives to be equatorial [14, 15, 19, 27], also predetermines the diequatorial *trans*-**4**-eq structure of trans-isomer of 2,3,3-trimethyl-3-silathiane 1-oxide. For the related *cis*-**4** isomer, the strong equatorial preference of the methyl group results in the higher stability of the *cis*-**4**-ax conformer as compared with the *cis*-**4**-eq form. However, because of a compromise between unfavorable interactions, $SO_{ax}/3\text{-}Me_{ax}$ in *cis*-**4**-ax and $2\text{-}Me_{ax}/(H_{4ax}$ and $H_{6ax})$ in *cis*-**4**-eq, both conformers are accessible, which results in their equilibrium.

Hopefully, these results will provide a better understanding of the chemical behavior of organosilicon cyclic sulfoxides in further investigations.

EXPERIMENTAL

^{1}H (400.13 MHz), ^{13}C (100.61 MHz) and ^{29}Si (79.49 MHz) NMR spectra of compounds **3**, *cis*-**4** and *trans*-**4** in $CDCl_3$ were obtained on a Bruker DPX 400 spectrometer and were referenced to TMS with residual protonated chloroform as the internal reference ($\delta_H = 7.25$ ppm, $\delta_C = 77.0$ ppm). Assignments of the ^{1}H and ^{13}C chemical shifts were based on the use of the shift parameters found for conformationally homogeneous thiane 1-oxide derivatives [16–19] as well as on ^{13}C NMR spectra with heteronuclear J-modulation of spin echo, two-dimensional (2D) and homonuclear (HMQC, COSY, TOCSY) correlation experiments. The low-temperature ^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2–$CDCl_3$–CCl_4 (4:2:1). Column chromatography was carried out using silica gel 60 (0.063–0.200 mm, ICN Biomedical Inc.). Analytical thin-layer chromatography was performed on Merck silica gel plates (60 F-254).

3,3-Dimethyl-3-silathiane 1-Oxide (3) This was obtained as described previously by oxidation of the corresponding 3-silathiane with *m*-chloroperbenzoic acid in CH_2Cl_2 [9] and purified by column chromatography [SiO_2, diethyl ether–methanol (8:1)]. ^{29}Si NMR ($CDCl_3$): $\delta = 0.00$ ppm.

cis- and trans-2,3,3-Trimethyl-3-silathiane 1-Oxides (*cis*-**4** and *trans*-**4**) (1:2) These were prepared by oxidation of the cyclic sulfide in a similar way [22]. Pure *cis*-**4** and *trans*-**4** diastereomers were isolated by column chromatography [SiO_2, hexane → hexane–diethyl ether (7:1) → diethyl ether–methanol (8:1)].

cis-2,3,3-Trimethyl-3-silathiane 1-Oxide (cis-4) This was isolated as a colorless oil, R_f 0.74 [diethyl ether–methanol (8:1)]. Analysis: calcd (%) for $C_7H_{16}SSiO$: C 47.68; H 9.14; S 18.18; Si 15.93; found: C 47.43; H 9.16; S 18.33; Si 15.42. ^{29}Si NMR ($CDCl_3$): $\delta = 1.88$ ppm.

trans-2,3,3-Trimethyl-3-silathiane 1-Oxide (trans-4) This was obtained as a colorless oil, R_f 0.60 [diethyl ether–methanol (8:1)]. Analysis: calcd (%) for $C_7H_{16}SSiO$: C 47.68; H 9.14; S 18.18; Si 15.93; found: C 48.35; H 9.35; S 17.75; Si 15.30. ^{29}Si NMR ($CDCl_3$): $\delta = 3.88$ ppm.

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