ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 2, pp. 253–263. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © E.N. Suslova, I.A. Ushakov, B.A. Shainyan, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 2, pp. 280–290.

Comparative Reactivity of Substituted 1,3- and 1,4-Thiasilinane *S*-Oxides in the Sila-Pummerer Rearrangement and Inversion of the Thiocarbonyl Group

E. N. Suslova, I. A. Ushakov, and B. A. Shainyan

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: bagrat@irioch.irk.ru

Received September 14, 2006

Abstract — The thermal sila-Pummerer rearrangement of diastereomeric 2,3,3-trimethyl-1,3-thiasilinane S-oxides was studied. Introduction of the methyl group in the 2 position of 3,3-trimethyl-3-thiasilinane *S*-oxide slows down the rearrangement. When heated in CCl_4, the *trans* isomer (2-Me_{eq}, SO_{eq}) converts into the *cis* isomer (2-Me_{eq}, SO_{ax}) which rapidly rearranges into 2,2,7-trimethyl-1,6,2-oxathiasilepane. On the contrary, the isomeric 2,4,4-trimethyl-1,4-thiasilinane *S*-oxide is thermally stable up to 160°C in DMSO. The inversion at the sulfur atom in 2,3,3-trimethyl-1,3-thiasilinane *S*-oxides and 2,4,4-trimethyl-1,4-thiasilinane *S*-oxides under the action of triethyloxonium tetrafluoroborate was studied. The *trans* isomer of 2,3,3-trimethyl-1,3-thiasilinane *S*-oxide (2-Me_{eq}, SO_{eq}) forms with $Et_3O^+BF_4^-$ a salt which decomposes in two ways. The first involves recovery of the starting sulfoxide due to SN2 substitution at the carbon atom of the ethoxy group, and the second, convertion into the *cis* isomer (2-Me_{eq}, SO_{ax}) which rearranges into 2,2,7-trimethyl-1,6,2-oxathiasilepane. Under the same conditions, the *cis* isomer of 2,3,3-trimethyl-1,3-thiasilinane *S*-oxide (2-Me_{eq}, SO_{eq}) decomposes to form siloxanes. *trans*-2,4,4-Trimethyl-4-thiasilinane *S*-oxide (2-Me_{eq}, SO_{eq}) under the action of $Et_3O^+BF_4^-$ convers into the *cis* isomer (2-Me_{eq}, SO_{ax}). The B3LYP/6-311G(d,p) theoretical analysis showed that the thermal inversion at the sulfur atom in the compounds studied has a high energy barrier.

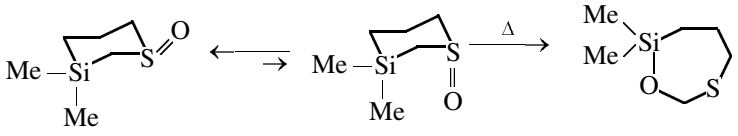
DOI: 10.1134/S1070363207020119

Cyclic organosilicon sulfoxides containing two heteroatoms of different nature in the ring are interesting objects for investigation of chemical properties and stereoelectronic interactions, as well as for conformational analysis. The first representatives of thiasilinane *S*-oxides, 3,3-dimethyl-1,3-thiasilinane *S*-oxide and 2,3,3-trimethyl-1,3-thiasilinane *S*-oxide, were synthesized by us about 10 years ago [1, 2]. Later 4,4-dimethyl-1,4-thiasilinane *S*-oxide [3], 2,2,3,3-tetramethyl-1,3-thiasilinane *S*-oxide, 2,4,4-trimethyl-1,4-thiasilinane *S*-oxide, and 2,4,4,6-tetramethyl-1,4-thiasilinane *S*-oxide were obtained [4], some of their diastereomers were separated and isolated individual, and their stereochemistry was studied [5, 6]. A series of works on the conformational analysis of various Si-substituted 1,4-thiasilinane *S*-oxides was also performed [7–10].

Of special interest among reactions of α-silylated sulfoxides $R_3SiCH_2S(O)R'$ is the sila-Pummerer rearrangement, that is, their conversion into *O*-silylated *O*,*S*-acetals R_3SiOCH_2SR' via 1,3-migration of silicon to oxygen. The sila-Pummerer rearrangement in acyclic sulfoxides is well known, and factors affecting its facility are thoroughly studied [11–19]. The main factors are the steric effects of substituents at the α-carbon atom, electronic effects of substituent at the sulfur atom, and sulfoxide stereochemistry. Substituents at the α-carbon atom, shielding the S=O group slow down [15, 16] or completely suppress [17] the rearrangement. Increase of the sulfoxide basicity facilitates silyl migration, so that alkyl sulfoxides (except for R' = *t*-C_4H_9) rearrange even in the cold [18, 19], whereas aryl sulfoxides rearrange only upon heating [14, 16].

Stereochemistry of the Si–C–S=O fragment in the starting sulfoxide plays the key role [13, 18–20]. A necessary condition for successful rearrangement is *syn*-planar arrangement of the Si–C and S=O bonds, which favors interaction between silicon and oxygen [19]. The effect is the most pronounced in cyclic sulfoxides with an exocyclic silicon atom, which are thermally stable only in the *E* configuration, that is, in the case of *anti*-planar arrangement of the Si–C and S=O bonds [20–22].

The information on the sila-Pummerer rearrangement of cyclic organosilicon sulfoxides are restricted to our work [23] on the conversion of 3,3-dimethyl-1,3-thiasilinane *S*-oxide (**I**) existing preferentially (>95%) in equatorial form **I**e [5] into 2,2-dimethyl-1,6,2-oxathiasilepane (**II**) via axial isomer **I**a upon heating at 60–70°C in THF or CCl_4. The mechanism of this rearrangement we recently studied theoretically [24].

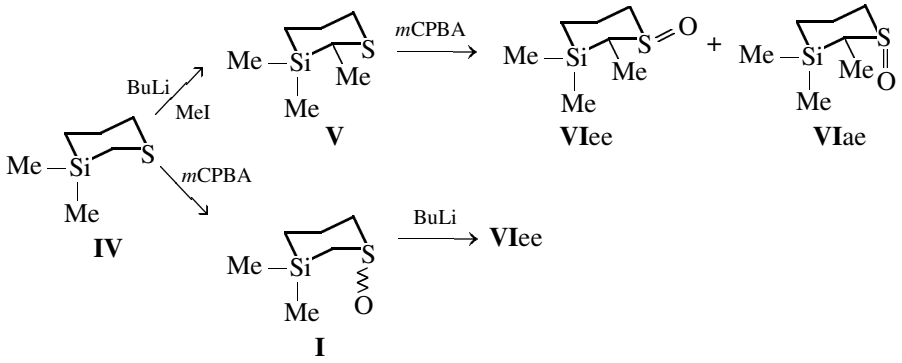


Ie **I**a **II** (1)

Proceeding with this research, in the present paper we have studied the sila-Pummerer rearrangement of diastereomeric 2,3,3-trimethyl-1,3-thiasilinane *S*-oxides and compared the resulting data with those for α-unsubstituted sulfoxide **I**. The rearrangement of sulfoxide **I** slowly proceeds even at room temperature: When a pure compound is kept for 3–5 days, ca. 5–7% of rearrangement product **II** forms (^{1}H NMR data). After longer keeping, formation of siloxane $[MeS(O)(CH_2)_3Si(Me_2)]_2O$ (**III**) is observed. In chloroform, sulfoxide **I** fails to rearrange within 2 weeks at room temperature, but suffers decomposition to siloxane **III**. The latter was isolated by column chromatography and fully characterized. Probably, the rearrangement in chloroform at room temperature is prevented by S=O···H–CCl_3 hydrogen bonding.

Diastereomeric 2,3,3-trimethyl-1,3-thiasilinane *S*-oxides were prepared by two protocols: lithiation–methylation of 3,3-dimethyl-1,3-thiasilinane (**IV**) to 2,3,3-trimethyl-1,3-thiasilinane (**V**) [25] followed by its oxidation to a mixture of the *trans* (**VI**ee) (major) and *cis* (**VI**ae) (minor) isomers of 2,3,3-trimethyl-1,3-thiasilinane *S*-oxide [5] or by oxidation of compound **IV** to sulfoxide **I** whose lithiation–methylation selectively provides *trans* isomer **VI**ee [4] (Scheme 1).

Scheme 1.

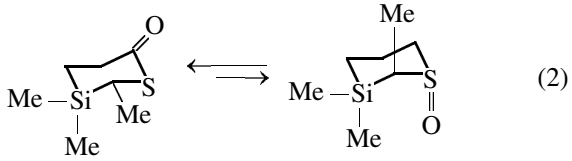


*m*CPBA = *m*-$ClC_6H_4CO_3H$.

The diastereomeric mixture was separated by column chromatography to obtain individual *trans* isomer **VI**ee, *cis* isomer **VI**ae, and a fraction enriched with *cis* isomer **VI**ae. To compare the reactivity of isomers **VI**ae and **VI**ee, their sila-Pummerer rearrangement was studied by the method of competitive reactions using the examples of pure *trans* isomer **VI**ee and a 2 : 1 mixture of isomers **VI**ae and **VI**ee. It should be emphasized that the sila-Pummerer rearrangement of axial cyclic sulfoxides was studied here for the first time; so far such compounds could not be obtained, since the axial isomers rearranged in statu nascendi upon oxidation of the corresponding sulfides [13, 20, 22].

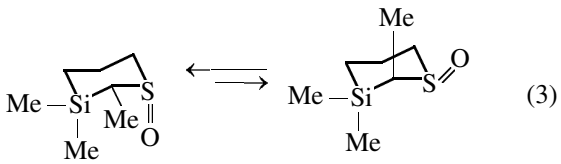
It is noteworthy for subsequent analysis that *trans* isomer **VI**ee and *cis* isomer **VI**ae with an equatorial 2-methyl group, while being major conformers, exist,

according to [5], in equilibrium with minor conformers **VI**aa and **VI**ea [Eqs. (2) and (3)].



(2)

VIee **VI**aa



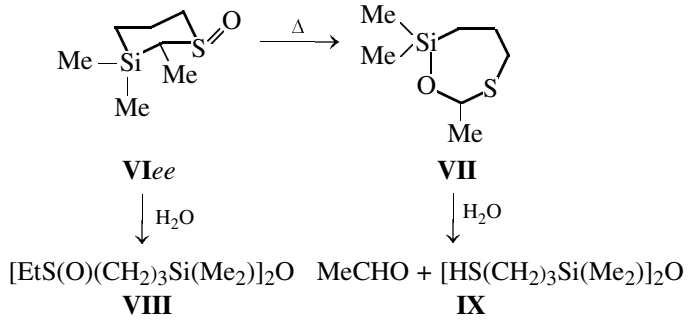
(3)

VIae **VI**ea

Unlike unsubstituted sulfoxide **I**, a pure *trans* isomer of 2-methyl-substituted sulfoxide **VI**ee, according to ^{1}H NMR data, does not rearrange at room temperature but fairly slowly decomposes to siloxanes under the action of air moisture (by 75% after 2 weeks). The higher stability of sulfoxide **VI**ee compared to sulfoxide **I** is consistent with the known fact that the sila-Pummerer rearrangement slows down with increasing number of substituents at the α-carbon atom in α-silylated sulfoxides [15–17]. The rearrangement product was detected neither sulfoxide **VI**ee was kept in chloroform for one month at –18°C nor even after it was heated in CCl_4 at 65°C for 1.5 h.

The rearrangement product, 2,2,7-trimethyl-1,6,2-oxathiasilepane (**VII**), appears in appreciable amounts (~10%) only after a solution of *trans* isomer **VI**ee in CCl_4 has been heated at 50–75°C for 3–4 h. Its structure is proved by the appearance in the ^{1}H NMR spectrum of a new doublet of the CH_3 group at 1.5 ppm and the corresponding quartet of the methine proton at 5 ppm. Such position of the methine proton signal is characteristic of the SCHOSi fragment and virtually coincides with the position of the SCH_2O group signal in rearrangement product **II** (4.9 ppm) [23]. ^{1}H NMR monitoring showed that only on further heating of the solution for 5 h at 80°C the conversion of **VI**ee reaches 90%. Therewith, the reaction is complicated by the decomposition of sulfoxide **VI**ee to siloxane $[EtS(O)\cdot(CH_2)_3Si(Me_2)]_2O$ (**VIII**), as well as by the decomposition of rearrangement product **VII**, involving, by analogy with [23], elimination of acetaldehyde. Siloxane **VIII** was isolated by column chromatography and fully characterized. In view of Eq. (2), the general scheme of transformations can be represented as follows (Scheme 2).

Scheme 2.



VI*ee* **VII**

VIII **IX**

The formation of mercaptosiloxane **IX** is evidenced by the presence in the ^{1}H NMR spectrum of signals which coincide with those of the pure sample isolated in [23]. The content of rearrangement product **VII** reaches ca. 40%, and the **VII** : **VI**e : siloxanes ratio is 3.5 : 1 : 5. We failed to isolate pure compound **VII** by column chromatography, since it partially decomposed on silica due to the lability of the Si–O–C bond.

The rearrangement of *cis* isomer **VI**ae with an axial S=O group proceeds much easier. Even at room temperature after 1 day it rearranges to product **VII** almost completely, with concurrent decomposition to siloxanes. Even in a chloroform solution at room temperature, up to 12% of rearrangement product **VII** and 24% of siloxanes formed within 6 days.

By ^{1}H NMR spectroscopy we studied the dynamics of the rearrangement at various temperatures by the method of competitive reactions with a 2 : 1 mixture of **VI**ae and **VI**ee in CCl_4. The relative contents of **VI**ae, **VI**ee, and **VII** in the solution were determined from the integral intensities of the most characteristic signals: doublets of the 2-Me groups at 1.30, 1.35,

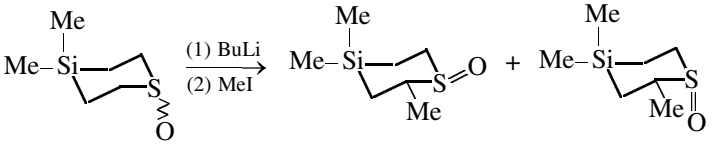
and 1.45 ppm in **VI**ae, **VI**ee, and **VII**, respectively, a quartet of the methine proton at 5 ppm in **VII**, as well as 6-H_{eq} signals in isomers **VI**ae and **VI**ee and a low-field signal of the 7-CH_2 group in **VII** with characteristic multiplet splittings. The rearrangement proceeds to an appreciable extent only at 55°C: after 2.5 h, ca. 7% of product **VII** forms. At 65°C after 1 h, its content reaches 26%, and the **VI**ae : **VI**ee ratio varies from 2 : 1 to 1.6 : 1. Taking into account that *trans* isomer **VI**ee scarcely rearranges at this temperature, we can conclude that under these conditions rearrangement product **VII** is formed exclusively from *cis* isomer **VI**ae. Upon further heating to 70°C, the content of product **VII** reaches 54%, and the **VI**ae : **VI**ee ratio changes to 1 : 1. The decrease of the content of isomer **VI**ee in the reaction mixture is caused by its partial decomposition to siloxane.

Analysis of integral intensities in the course of heating of the CCl_4 solution of the mixture of isomers **VI**ae and **VI**ee at 80°C showed that the initial **VIII** : **VI**ae : **VI**ee ratio of 0 : 70 : 30, becomes 10 : 45 : 45, 22 : 26 : 52, 31 : 15 : 54, and 45 : 9 : 46 after 10 min, 1 h, 1.5 h, and 2.5 h, respectively. These data are indicative of the fact that rearrangement product **VIII** forms almost exclusively from *cis* isomer **VI**ae. However, the **VI** → **VII** conversion cannot be radically increased by elevated temperature, since under these conditions the content of siloxanes in the reaction mixture reaches 70%, that is, considerably exceeds their amount in the rearrangement of pure *trans* isomer **VI**ee. This result provides evidence to show that *cis* isomer **VI**ae easier, due to its lower stability, decomposes to siloxanes than *trans* isomer **VI**ee.

The above analysis allows us to suggest that the thiasilinane *S*-oxides studied undergo the sila-Pummerer rearrangement either due to the axial S=O group in starting *cis* isomer **VI**ae, or, in the case of *trans* isomer **VI**aa, the percentage of the minor axial sulfoxide is increased by heating. The alternative pathway which includes thermal configuration inversion at the sulfur atom, should probably be ruled out, the more so as the configurational stability of sulfoxides has long been known [26]. Theoretical analysis of factors affecting the barrier to pyramidal inversion at the heteroatom showed that introduction of bulky and electronegative substituents, conjugation of the lone pair of the heteroatom with the π system or *d* orbitals of the substituent, as well as enhanced angular strain lower the barrier to inversion [27]. In the absence of factors significantly stabilizing the transition state for sulfur inversion, racemization of sulfoxides with alkyl and/or aryl substituents is characterized by a high activation enthalpy $\Delta H^{\neq}$ 35–42 kcal mol^{-1} and nearly zero activation entropy $\Delta S^{\neq}$ and proceeds only under severe conditions (~200°C) [26]. Arenethiolsulfinates ArS(O)SAr [28], vinyl sulfoxides with electron-acceptor groups at the double bond [29], and allyl sulfoxides $ArS(O)CH_2CH{=}CH_2$ [29] racemize much easier; in these cases, the transition state is stabilized by the interaction of the lone electron pair of the sulfinyl sulfur atom with vacant orbitals of the sulfenyl sulfur atom [28], conjugation of the lone electron pair with the electron-deficient double bond [29], or interaction of the sulfoxide oxygen atom with the C=C bond to form *O*-allyl arenesulfenate $ArS{-}OCH_2CH{=}CH_2$ [30]. The racemization of benzyl sulfoxides, too, proceeds much easier, but it follows another mechanism: ratedetermining homolytic dissociation of the S–CH_2 bond and fast intracage recombination of the radicals formed, which is evidenced by the high positive activation entropy [31]. A DFT theoretical analysis of the racemization of methanesulfinyl chloride MeS(O)Cl showed that the configuration inversion at the sulfur atom occurs easily when catalyzed by triethylamine, and this process can be a key step in the synthesis of optically active sulfoxides from diacetone-Dglucose [32].

The thermal inversion of configuration at the sulfur atom in sulfoxides **I** and **VI** is impossible to study, since they rearrange and decompose to siloxanes, unlike the situation with their isomeric 1,4-thiasilinane *S*-oxide derivatives which are much more stable thermally.

Diastereomeric 2,4,4-trimethyl-1,4-thiasilinane *S*-oxides (**XI**) were prepared by lithiation–methylation of 4,4-dimethyl-1,4-thiasilinane *S*-oxide (**X**) [4]. *trans* Isomer **XI**ee with equatorial thiocarbonyl and 2-methyl groups is formed as the major diastereomer, and *cis* isomer **XI**ae with an axial thiocarbonyl group and an equatorial 2-methyl group as the minor one. Isomers **XI**ee and **XI**ae were isolated by column chromatography [4, 6].

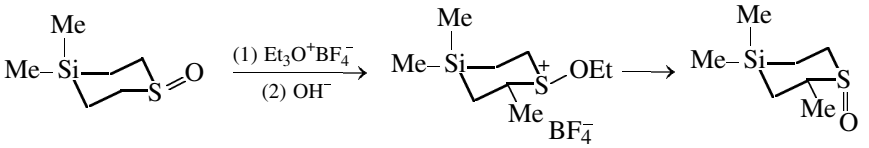


X **XI**ee, base **XI**ae, minor (4)

The **XI**ee : **XI**ae ratio in the mixture remains unchanged after storage during half a year at room temperature or after reflux in a $CDCl_3$ solution for 2 h. Unlike its isomer **VI**ee, 2,4,4-trimethyl-1,4-thiasilinane *S*-oxide (**XI**ee) undergoes no transformations not only upon reflux in CCl_4 but also upon heating at 165°C for 2 h in DMSO. Further heating at 180°C during 7 h leads to its decomposition to cyclic siloxanes $[Si(Me_2)_2O]_n$, as evidenced by the presence in the ^{1}H NMR spectrum of a single Me_2Si proton signal at 0.08 ppm. This fact is provides independent evidence for the suggestion that the easiness of the **I** → **II** and **VI** → **VII** rearrangement is caused by the proximity of the oxygen and silicon atoms in axial sulfoxides **Ia**, **VI**aa, and **VI**ae and for our earlier suggested intramolecular mechanism of the sila-Pummerer rearrangement [24].

Compared to thermal isomerization of sulfoxides, their chemical isomerization by formation of alkoxysulfonium salts upon O-alkylation, for example, with trialkyloxonium tetrafluoroborate, with subsequent alkaline hydrolysis occurs much easier. The reaction involves retention of configuration at the stage of formation of alkoxysulfonium salt and with inversion of configuration at the stage of hydrolysis by the mechanism of S$_N$2 substitution at the sulfur atom [33]. Such approach allows one to accomplish inversion of configuration in sulfoxides and was successfully realized both with acyclic and cyclic sulfoxides [33–35].

We examined the possibility of inversion of configuration at the sulfur atom in *trans*-2,4,4-trimethyl-1,4-thiasilinane *S*-oxide (**XI**ee). Upon reaction with $Et_3O^+BF_4^-$ at room temperature with subsequent treatment with NaOH it easily affords the isomerization product which was isolated by column chromatography and turned out to be identical to the minor diastereomer **XI**ae formed by reaction (4).



XIee **XII** **XI**ae (5)

Intermediate salt **XII** was obtained as a crude product and characterized by NMR spectroscopy. The structure is proved by the presence in the ^{1}H NMR spectrum of signals of the ethoxy group (triplet of CH_3 protons at 1.43 ppm and two multiplets of diastereotopic OCH_2 protons at 4.42 and 4.52 ppm) and a doublet of the CH_3 group in the 2 position of the heterocycle, shifted by 0.15 ppm downfield as compared to sulfoxide **XI**ee. The spectrum of salt **XII** was performed by its comparison with the spectrum of the parent compound **XI**ee with account for signal multiplicities and integral intensities.

The **XI**ee → **XI**ae inversion in methylene chloride at room temperature proceeds by 50% after 1 h and by 70% after 5 h. Further increase of the duration of the process does not increase of the content of *cis* isomer **XI**ae in the reaction mixture. After decomposition of salt **XII**, the **XI**ee : **XI**ae ratios after 1- and 5-h reactions were 1 : 1 and 2.3 : 1, respectively. Isomers **XI**ee and **XI**ae were isolated by column chromatography, and their NMR spectra were consistent with those described earlier [4, 6].

Inversion at the sulfur atom in the equatorial isomer of *trans*-2,3,3-trimethyl-3-thiasilinane *S*-oxide (**VI**ee) was of interest as a possible route to hardly accessible *cis* isomer **VI**ae, since *trans* isomers of 2-substituted 3,3-dimethyl-1,3-thiasilinane *S*-oxides are prepared in good yields, as shown in Scheme 1. However, the reaction of compound **VI** with $Et_3O^+BF_4^-$ in CH_2Cl_2 neither as a pure *trans* isomer **VI**ee nor as a mixture with *cis* isomer **VI**ae involved inversion at the sulfur atom. NMR monitoring of the process showed that *trans* isomer **VI**ee forms with $Et_3O^+BF_4^-$ salt **XIII** (Scheme 3), which is corroborated by the downfield shift of characteristic signals in the ^{1}H NMR spectrum. The largest shift (0.6–0.7 ppm) is observed for H^{2ax} and H^{6ax}, which are most proximate to the cationic center, and the shift of the H^{6eq} signal is slightly smaller (0.4 ppm) Characteristic multiplicities of the signals are therwith preserved. The signal of the 2-CH_3 group shifts downfield by 0.14 ppm.

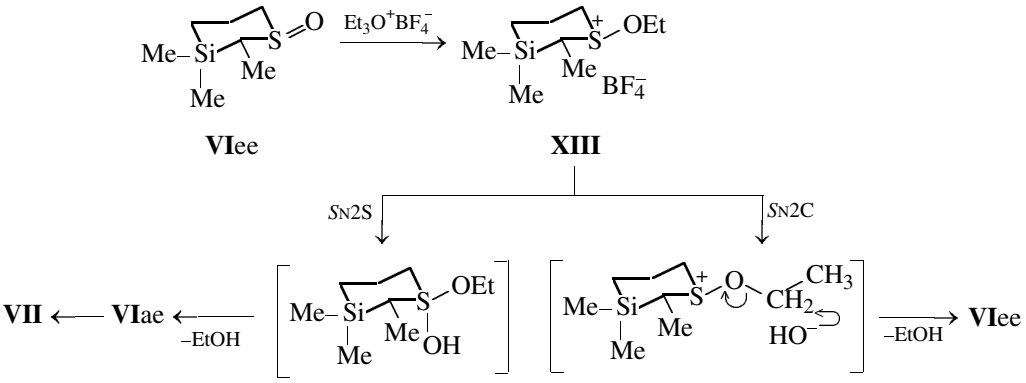
Alkaline hydrolysis of salt **XIII** with aqueous NaOH affords 46% of starting sulfoxide **VI**ee, 28% of rearrangement product **VII**, and 26% of decomposition products, viz. siloxanes. The major decomposition product and the only one isolated by column chromatography was siloxane **VII**. Attempted decom-

position of salt **XIII** under the same conditions with softer bases, K_2CO_3 or NH_4HCO_3, only slightly changed the composition of the products, while the content of siloxanes slightly decreased. As the decomposition temperature was decreased to 8°C, the content of siloxanes substantially, more than two times, decreased.

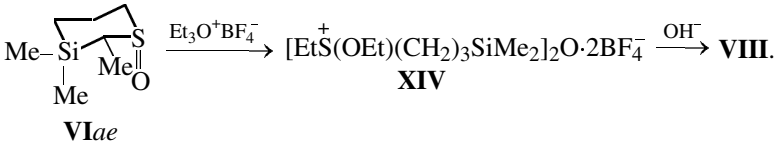
In view of our previous results [23, 24], seven-membered ring **VII** can be tentatively considered to result from fast sila-Pummerer rearrangement of salt **XIII** formed initially from *cis* isomer **VI**ae, due to the proximity of the oxygen and silicon atom in its molecule to each other.

Starting sulfoxide **VI**ee is probably recovered through base attack on the α-carbon atom of the ethoxy group in salt **XIII** [33] (in Scheme 3, siloxanes are omitted for simplicity).

Scheme 3.



Investigation of the reaction of $Et_3O^+BF_4^-$ with 1 : 1 and 2 : 1 mixtures of isomers **VI**ee and **VI**ae provided additional information concerning the inversion and rearrangement processes. According to ^1H NMR data, already after 40 min *cis* isomer **VI**ae is completely consumed, but the only salt formed is salt **XIII** produced from *trans* isomer **VI**ee. No second set of characteristic signals of the H^{2ax}, H^{6ax}, H^{6eq}, and 2-CH_3 protons, that would be expected in the case of formation of the ethoxysulfonium salt from *cis* isomer **VI**ae, was observed in the spectrum. Moreover, much siloxanes are formed. The ^1H NMR spectrum contains signals which could be tentatively assigned to the linear disiloxane salt $\{[EtS(OEt)(CH_2)_3SiMe_2]_2O\}^{2+}\cdot 2BF_4^-$ (**XIV**) (two signals of the $SiMe_2$ group at 0.26 and 0.28 ppm and a triplet of the SCH_2CH_3 group at 1.5 ppm), but, because of the overlap with complex multiplets belonging to protons of other groups, these signals proved impossible to assign reliably. The rapid disappearance of *cis* isomer **VI**ae, the absence of its ethoxysulfonium salt, as well as the doubled amount of siloxanes as compared to the reaction with pure *trans* isomer **VI**ee suggest that *cis* isomer **VI**ae easily decomposes, already at the stage of reaction with $Et_3O^+BF_4^-$, to salt **XIV** whose alkaline hydrolysis affords siloxane **VII**.

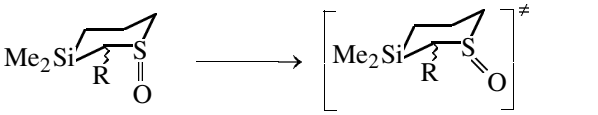


(6)

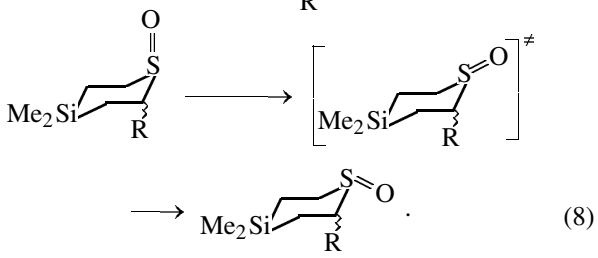
Therewith, 23% of starting *trans* isomer **VI**ee is recovered from the reaction mixture, and 27% of rearrangement product **VII** and 50% of siloxanes are formed. The major compound among the siloxanes, like in reaction with pure transisomer **VI**ee, is siloxane **VII**. Under the conditions of alkaline hydrolysis, *trans* isomer **VI**ee is so stable that can be recovered in the pure form. Rearrangement product **VII** is less stable; however, it was unequivocally identified in the crude product by NMR. These results are in

qualitative agreement with published data which show that O-silylated thioacetals withstand treatment with 5% aqueous alkali [36].

We performed a theoretical assessment of the barriers to thermal inversion of the S=O group in the cyclic organosilicon sulfoxides studied, by means of calculation of transition states for the transformation of their axial isomers to equatorial ones:



(7)

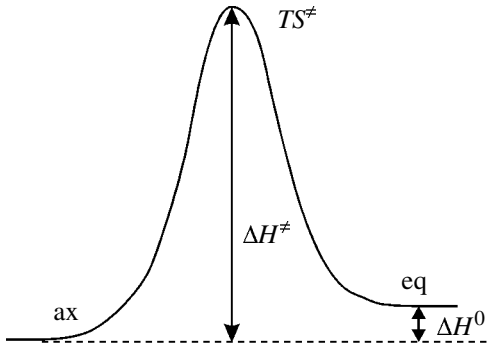


(8)

The calculations of individual conformers and transition states were performed at the B3LYP/6-311G(d,p) level of theory with the Gaussian-03 suite of programs (B.03 version) [37]. The geometry of transitions states was optimized in the "Tight" mode; the transition states all have a single imaginary vibration. Analysis of the shape of this vibration provides evidence to show that the calculated transition states connect the axial and equatorial conformers of the sulfoxides. The energy profile of S=O inversion, depicted in the figure below, practically does not depend neither on the relative position of heteroatoms nor on the presence or orientation of the substituent in the ring.

Some calculated characteristics for the conformers and transition states are given in the table.

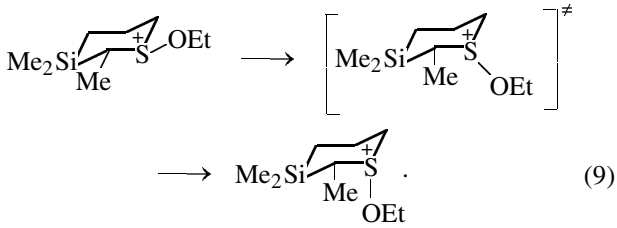
The S–O bond in axial sulfoxides is 0.002–0.006 Å longer than in equatorial due to $\sigma(C–H_{ax}) \rightarrow \sigma^*(S=O)$ stereoelectronic interactions. This is proved, in particular, by the fact that the axial methyl group decreases the Δl(S–O) value. In the transition state, there is a substantial, by ~0.04 Å, elongation of the S–O bond coplanar to the C–S–C plane ($\Sigma\alpha$ ~360o, see table). The Si–C(2) bond length in axial α-sulfoxide **VI**ae is 1.920 Å that is 0.007 Å longer than in its equatorial isomer **VI**ee. This is indicative of a more facile decomposition of *cis* isomer **VI**ae with rupture of the Si–C(2) bond, and is in line with the experimental observations.



The weak endothermic effect for the $SO_{ax} \rightarrow SO_{eq}$ inversion reflects a somewhat higher stability of the axial conformer in the gas phase. In solution, due to the large dipole moment, the equatorial sulfoxides are more stable (cf. [38] and references therein).

The fact that the energetic parameters of the inversion process, as well as the geometric and vibrational parameters of the transition state are virtually independent on the structure of the sulfoxide suggests that the obtained characteristics of the process are general for all cyclic sixmembered sulfoxides and confirm that in the absence of nucleophilic catalysis or strong nonspecific interaction with solvent (due to a higher dipole moment of the transition state as compared to those of both conformers) the inversion is hindered.

The above assumption that the recovery of starting sulfoxide **VI**ee from salt **XIII** is the result of nucleophilic attack on the α-carbon atom of the ethoxy group (Scheme 3), is likely to be true only if the formation of the salt does not reduce the barrier to inversion at the sulfur atom to very small values, when spontaneous racemization at room temperature is possible. To verify this option, we calculated the inversion in the cation of ethoxysulfonium salt **XIII**:



(9)

The results are shown in the table. Noteworthy, the salt formation substantially, by 0.033 Å for *cis* isomer **VI**ae and by 0.050 Å for *trans* isomer **VI**ee, elongates the Si–C(2) bond, that is, drastically weakens it. The ease of Si–C(2) bond rupture in cyclic organosilicon α-sulfoxides, especially in isomers with an axial S=O group (due to the proximity of the oxygen and silicon atoms to each other), is responsible for the impossibility of the interconversion of axial and equatorial

Total energies (E), dipole moments (μ), S–O bond lengths (l_{S-O}), sums of the angles at the sulfur atom ($\Sigma\alpha$), thermal effect (ΔH^0) and barriers to S=O inversion ($\Delta H^{\neq}$) in 2-R-3,3-dimethyl-3-thiasilinane *S*-oxides, 2-R-4,4-dimethyl-4-thiasilinane *S*-oxides, and ethoxysulfonium salts **XIII**

Structure	R	$-E$, au	μ, D	l_{S-O}, Å	$\Sigma\alpha$, °	ΔH^0, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	ν, cm^{-1}
1,3-SO_{ax}	H	1000.115855	3.86	1.518	310.5			
1,3-SO_{eq}		1000.112297	5.02	1.512	304.6	9.3	199.2	
1,3-SO ($TS^{\neq}$)		1000.040000	5.97	1.557	359.9			567*i*
1,3-SO_{ax}	Me_{ax}	1039.437155	3.93	1.520	312.8			
1,3-SO_{eq}		1039.435557	4.78	1.516	312.7	4.2	188.4	
1,3-SO ($TS^{\neq}$)		1039.365395	5.65	1.558	359.9			550*i*
1,3-SO_{ax}	Me_{eq}	1039.438361	3.81	1.521	311.8			
1,3-SO_{eq}		1039.435008	4.82	1.515	310.7	8.8	197.2	
1,3-SO ($TS^{\neq}$)		1039.363240	5.71	1.558	359.8			555*i*
1,4-SO_{ax}	H	1000.112324	3.92	1.518	310.4			
1,4-SO_{eq}		1000.108797	5.07	1.514	309.3	9.2	199.7	
1,4-SO ($TS^{\neq}$)		1000.036266	6.01	1.560	359.9			566*i*
1,4-SO_{ax}	Me_{ax}	1039.435541	4.00	1.519	311.2			
1,4-SO_{eq}		1039.433822	4.83	1.517	311.0	4.5	192.9	
1,4-SO ($TS^{\neq}$)		1039.362066	6.00	1.558	359.9			544*i*
1,4-SO_{ax}	Me_{eq}	1039.438734	3.85	1.519	311.1			
1,4-SO_{eq}		1039.435954	4.85	1.516	309.5	7.3	195.8	
1,4-SO ($TS^{\neq}$)		1039.364146	5.74	1.561	359.9			557*i*
1,3-$^+SOEt_{ax}$	Me_{eq}	1118.458265		1.642	308.1			
1,3-$^+SOEt_{eq}$		1118.459340		1.645	305.6	–2.8	135.1	
1,3-$^+$SOEt ($TS^{\neq}$)		1118.406829		1.639	359.7			369*i*

sulfoxides via the stage of salt formation, as is the case in their organic analogs [33].

As follows from the table, the formation of salt **XIII** from *trans* isomer **VI**ee is 11.6 kJ mol^{-1} more energetically favorable than from *cis* isomer **VI**ae, which is apparently responsible for the absence of the latter in the ^{1}H NMR spectrum of the reaction mixture in the reaction of salt $Et_3O^+BF_4^-$ with a mixture of the isomers. Salt formation substantially, by a factor of 1.5, decreases the barrier to inversion, but it still remains very high (see table), which corroborates the assumption on the mechanism of the recovery of sulfoxide **VI**ee from salt **XIII**, depicted in Scheme 3.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 instrument in thin layer. The NMR spectra were registered on a Bruker DPX-400 spectrometer at 400 (^{1}H), 100 (^{13}C), and 80 MHz (^{29}Si) for solutions in $CDCl_3$, reference TMS. The structure of all new compounds was proved by the *j*-modulated ^{13}C NMR spectra. Column chromatography was performed on silica 60 [0.063–0.200 mm (Merck or ICN Biomedical)] and analytical TLC, on silica plates (Merck 60 F-254, visualization in iodine vapors). The melting points were determined on a Boetius hot stage (VEB Analytik). All reactions were carried out in argon with protection from air moisture. Solvents and reagents were dried and purified by standard protocols directly prior to use. Triethyloxonium tetrafluoroborate was prepared according to [39] and reprecipitated from methylene chloride into ether directly prior to use, mp 88–91°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 t (3H, Me), 3.73 q (2H, CH_2O).

1,1,3,3-Tetramethyl-1,3-bis[3-(methylsulfinyl)-propyl]disiloxane (III). Pure 3,3-dimethyl-1,3-thiasilinane *S*-oxide (**I**) was kept in a closed vessel at room temperature in the light for two weeks. From ^{1}H NMR data, the mixture formed contains ~50% of starting compound **I**, ~15% of rearrangement product **II**, and ~30% of siloxane **III**. The latter compound was isolated as a light yellow oil by column chromatography, eluents hexane–ether (7 : 1), ether–methanol (from 20 : 1 to 1 : 1, MeOH). R_f 0.61 (ether–methanol, 8 : 1). IR spectrum, ν, cm^{-1}: 2940, 1395, 1230, 1030, 1010, 820, 780. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.085 s (6H, $SiMe_2$), 0.63 m (1H, $SiCH^A$),

0.72 m (1H, $SiCH^B$), 1.80 m (2H, CCH_2C), 2.55 s (3H, MeS), 2.68 m (2H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –0.087 (SiMe), 16.52 (SiC), 17.27 (C*C*C), 38.12 (SMe), 57.55 (SCH_2). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: 8.53. Found, %: C 42.69; H 9.03; S 18.52; Si 16.18. $C_{12}H_{30}S_2Si_2O_3$. Calculated, %: C 42.10; H 8.77; S 18.71; Si 16.37.

2,2,7-Trimethyl-1,6,2-oxathiasilepane (VII). A 5% CCl_4 solution of 2,3,3-trimethyl-1,3-thiasilinane *S*-oxide (**VI**) as a pure *trans* isomer **VI**ee or as a mixture of isomers **VI**ee and **VI**ae was heated at 50–80°C, periodically analyzing the composition of the reaction mixture by ^1H NMR spectroscopy. Below is given the ^1H NMR spectrum of compound **VII** obtained for the reaction mixture **VII** : siloxanes : **VI**ee (40 : 50 : 10). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.06 s (6H, $SiMe_2$), 0.75 d.d.d.d (1H, H^{5A}, *J* 14.8, 6.8, 3.4, 1.3 Hz), 1.49 d (3H, CH_3, *J* 6.2 Hz), 2.10 m (1H, H^{6A}), 2.64 m (1H, H^{7B}), 2.89 d d d d (1H, H^{7A}, *J* 14.6, 5.6, 3.1, 1.3 Hz), 5.02 q (1H, CH, *J* 6.2 Hz). The H^{5B} and H^{6B} signals at 0.6 ppm and 1.7 ppm, respectively, overlap with signals of siloxanes.

1,3-Bis[3-(ethylsulfinyl)propyl]-1,1,3,3-tetramethyldisiloxane (VIII) was isolated by column chromatography of the above reaction mixture as a reddish oily substance, eluents hexane, hexane–ether (20 : 1, 7 : 1), ether–methanol (20 : 1, 10 : 1, 8 : 1), and MeOH. R_f 0.83 (ether–methanol, 8 : 1). IR spectrum, ν, cm^{-1}: 2950, 1405, 1235, 1050, 1020, 825, 790. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.09 s (6H, $SiMe_2$), 0.62 d.d.d (1H, $SiCH^A$), 0.73 d d d (1H, $SiCH^B$, *J* 14.6, 10.8, 5.7 Hz), 1.34 t (3H, CH_3, *J* 7.5 Hz), 1.81 m (2H, CH_2), 2.69 m (4H, CH_2SOCH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 0.39 ($SiMe_2$), 6.86 (Me), 17.09 ($SiCH_2$), 17.91 (CH_2), 45.75 ($MeCH_2SO$), 55.13 ($OSCH_2$). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: 7.12. Found, %: C 44.82; H 9.30; S 17.37; Si 15.50. $C_{14}H_{34}S_2Si_2O_3$. Calculated, %: C 45.40; H 9.19; S 17.28; Si 15.19.

Reaction of *trans*-2,4,4-trimethyl-1,4-thiasilinane *S*-oxide (XIee) with triethyloxonium tetrafluoroborate. A mixture of 0.057 g of compound **XI**ee and 0.1 g of triethyloxonium tetrafluoroborate in 1.5 ml of CH_2Cl_2 was stirred for 1 h at room temperature, and the solvents were then evacuated. The ^1H NMR spectrum of the oily residue showed the presence of **1-ethoxy-2,4,4-trimethyl-1,4-thiasilinan-1-ium tetrafluoroborate (XII)** mixed with siloxanes. ^1H NMR spectrum of salt **XII** ($CDCl_3$), δ, ppm: 0.14 s (3H, SiMe), 0.21 s (3H, SiMe), 1.13 d.d (1H, H^{3a}, *J* 15.6, 12.1 Hz), 1.34 m (3H, $H^{5a} + H^{5e} + H^{3e}$), 1.43 t (3H, CH_3, *J* 7.0 Hz), 1.61 d (3H, CH_3, *J* 6.6 Hz), 3.66 m (2H, $H^{6a} + H^{2a}$), 4.05 m (1H, H^{6e}), 4.42 m (1H, OCH^B), 4.52 m (1H, OCH^A). Salt **XII** was decomposed by adding to the residue after removal of the solvents 3 ml of water and 1 N aqueous NaOH (dropwise) to pH 10–11. The mixture was then diluted with saturated brine, extracted with CH_2Cl_2 (3 × 3 ml), and dried over anhydrous $MgSO_4$. The solvents were removed to obtain 0.05 g (80%) of a crude product. Its ^1H NMR spectrum showed the presence of isomers **XI**ee and **XI**ae in a 1 : 1 ratio. Column chromatography, eluents hexane, hexane–ether (21 : 3), ether-methanol (from 20 : 0.5 to 8 : 1) gave 5 mg of *cis* isomer **XI**ae, 4 mg of a mixture of isomers **XI**ee and **XI**ae in a 1 : 7 ratio, and 8 mg of pure crystalline isomer **XI**ee, mp 54–55°C.

Reaction of 2,3,3-trimethyl-1,3-thiasilinane *S*-oxide with triethyloxonium tetrafluoroborate. *a*. To a stirred solution of 0.32 g of triethyloxonium tetrafluoroborate in 5 ml of $CHCl_3$, 0.24 g of a solution of compound **VI**ee in 1 ml of $CHCl_3$ was added dropwise. The ^1H NMR spectrum taken after 40 min showed the absence of starting sulfoxide **VI**ee and presence of **1-ethoxy-2,3,3-trimethyl-1,3-thiasilinan-1-ium tetrafluoroborate (XIII)** and a small amount (~15%) of siloxanes. ^1H NMR spectrum of salt **XIII** ($CDCl_3$), δ, ppm: 0.23 s (3H, SiMe), 0.32 s (3H, SiMe), 0.76 d d d (1H, H_{4ax}, J_{4ax4eq} 15.0, J_{4ax5ax} 14.1, J_{4ax5eq} 4.9 Hz), 0.95 d.d.d.d (1H, H_{4eq}, *J* 15.0, 4.5, 3.2, 1.3 Hz), 1.23 t (3H, CH_3, *J* 7.0 Hz), 1.58 d (3H, CH_3, *J* 6.9 Hz), 1.88 m (1H, H_{5ax}), 2.46 d d d d (1H, H_{5eq}, *J* 15.9, 10.7, 5.1, 2.2 Hz), 2.91 q (1H, H_{2ax}, *J* 6.9 Hz), 3.17 t d (1H, H_{6ax}, J_{6ax6eq} 13.0, J_{6ax5ax} 13.0, J_{6ax5eq} 2.2 Hz), 3.51 q (2H, OCH_2, *J* 7.0 Hz), 3.64 m (1H, H_{6eq}).

b. To a stirred solution of 0.05 g of a mixture of sulfoxides **VI**ee and **VI**ae in a 2 : 1 ratio in 1 ml $CHCl_3$, a solution of 0.06 g of triethyloxonium tetrafluoroborate in 3 ml of CH_2Cl_2 was slowly added. The mixture was stirred for 2 h, the solvents removed under reduced pressure, and the residue was dried in a vacuum (1 mm Hg). The ^1H NMR spectrum of the residue showed the absence of the starting sulfoxides and presence of two ethoxysulfoxonium salts in a 1.7 : 1 ratio, mixed with ~30% of siloxanes.

Decomposition of 1-ethoxy-2,3,3-trimethyl-1,3-thiasilinan-1-ium tetrafluoroborate (XIII). After treatment with ether in the cold to remove all ether-soluble impurities, the suspension of 0.19 g of salt **XIII** in a mixture with 1.67 ml of H_2O and 6.67 ml of MeOH was cooled to +10°C, and a 0.1N solution of K_2CO_3 (23 ml) was added dropwise until a sustainable pink color (by phenolphthalein) appeared. The reaction mixture was extracted with CH_2Cl_2, the extract was dried over $MgSO_4$, and the solvent was

removed. According to ^{1}H NMR data, the residue contains 51% of sulfoxide **VI**ee, 27% of rearrangement product **VII**, and ~22% of siloxanes. Column chromatography on silica, eluents hexane, hexane–ether (20 : 1, 7 : 1), ether–methanol (from 20 : 1 to 8 : 1), starting sulfoxide **VI**ee (R_f 0.48, ether–methanol, 8 : 1), and siloxane **VII** (R_f 0.18 in the same system). The reaction mixture obtained from sulfoxides **VI**ee and **VI**ae was decomposed in a similar way. Column chromatography under the same conditions gave sulfoxide **VI**ee and siloxane **VII**.

ACKNOWLEDGMENTS

The authors are highly grateful to S.V. Kirpichenko for fruitful discussions of the results of the present work.

The work was financially supported by the Russian Foundation for Basic Research (project no. 04-03-32131).

REFERENCES

1. 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.
2. Tolstikova, L.L. and Shainyan, B.A., *Russ. J. Gen. Chem.,* 1997, vol. 67, no. 11. P. 1728.
3. Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *Russ. J. Gen. Chem.,* 2005, vol. 75, no. 8, p. 1234.
4. Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *Russ. J. Gen. Chem.,* 2006, vol. 76, no. 1, p. 103.
5. Kirpichenko, S.V., Albanov, A.I., and Pestunovich, V.A., *J. Sulfur Chem.,* 2004, vol. 25, no. 1, p. 21.
6. Shainyan, B.A., Ushakov, I.A., and Suslova, E.N., *J. Sulfur Chem.,* 2006, vol. 27, no. 1, p. 3.
7. Shainyan, B.A., Freeman, F., Asgari, N., Entezam, B., Gomarooni, F., Mac, J., Nguyen, M.H., Nguyen, N.N.T., Nguyen, T.P., Pham, N.B., Sultana, P., and Welch, T.S., *Int. J. Quant. Chem.,* 2005, vol. 101, no. 1, p. 40.
8. Freeman, F. and Shainyan, B.A., *Int. J. Quant. Chem.,* 2005, vol. 105, no. 4, p. 313.
9. Freeman, F., Entezam, B., Gomarooni, F., Welch, T.S., and Shainyan, B.A., *J. Organomet. Chem.,* 2005, vol. 690, no. 18, p. 4103.
10. Shainyan, B.A., *Int. J. Quant. Chem.,* 2006, vol. 107, no. 1, p. 189.
11. Brook, A.G., *Acc. Chem. Res.,* 1974, vol. 7, no. 3, p. 77.
12. Kwart, H., *Phosphorus Sulfur,* 1983, vol. 15, no. 3, p. 293.
13. Block, E. and Aslam, M., *Tetrahedron.,* 1988, vol. 44, no. 2, p. 281.
14. Brook, A.G. and Anderson, D.G., *Can. J. Chem.,* 1968, vol. 46, no. 12, p. 2115.
15. Carey F. A. Hernandez O., *J. Org. Chem.,* 1973, vol. 38, no. 15, p. 2670.
16. Ager D. J., *J. Chem. Soc., Perkin Trans. 1,* 1983, no. 4, p. 1131.
17. Kocienski, P.J., *Tetrahedron Lett.,* 1980, vol. 21, no. 16, p. 1559.
18. Vedejs, E. and Mullins, M., *Tetrahedron Lett.,* 1975, vol. 16, no. 24, p. 2017.
19. Barbaro, G., Battaglia, A., Giogianni, P., Maccagnani, G., Macciantelli, D., Bonini, B.F., Mazzanti, G., and Zani, P., *J. Chem. Soc., Perkin Trans. 1,* 1986, no. 2, p. 381.
20. Carey, F.A., Dailey, O.D., Hernandez, O., and Tucker, J.R., *J. Org. Chem.,* 1976, vol. 41, no. 25, p. 3975.
21. Bonini, B.F., Lenzi, A., Maccagnani, G., Barbaro, G., Giogianni, P., and Macciantelli, D., *J. Chem. Soc., Perkin Trans. 1,* 1987, no. 9, p. 2643.
22. Bonini, B.F., Mazzanti, G., Zani, P., and Maccagnani, G., *J. Chem. Soc., Perkin Trans. 1,* 1989, no. 11, p. 2083.
23. Kirpichenko, S.V., Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *Tetrahedron Lett.,* 1999, vol. 40, no. 1, p. 185.
24. Shainyan, B.A., Kirpichenko, S.V., and Freeman, F., *J. Am. Chem. Soc.,* 2004, vol. 126, no. 37, p. 11456.
25. Kirpichenko, S.V., Shainyan, B.A., Suslova, E.N., and Albanov, A.I., *Russ. J. Gen. Chem.,* 2003, vol. 73, no. 2, p. 321.
26. Rayner, D.R., Gordon, A.J., and Mislow, K., *J. Am. Chem. Soc.,* 1968, vol. 90, no. 18, p. 4854.
27. Rauk, A., Allen, L.C., and Mislow, K., *Angew. Chem. Int. Ed. Engl.,* 1970, vol. 9, no. 6, p. 400.
28. Koch, P. and Fava, A., *J. Am. Chem. Soc.,* 1968, vol. 90, no. 14, p. 3867.
29. Yuste, F., Ortiz, B., Perez, J.I., Rodriguez-Hernandes, A., Sanchez-Obregon, R., Walls, F., and Ruano, J.L.G., *Tetrahedron,* 2002, vol. 58, no. 13, p. 2613.
30. Bickart, P., Carson, F.W., Jacobus, J., Miller, E.G., and Mislow, K., *J. Am. Chem. Soc.,* 1968, vol. 90, no. 18, p. 4869.
31. Miller, E.G., Rayner, D.R., Thomas, H.T., and Mislow, K., *J. Am. Chem. Soc.,* 1968, vol. 90, no. 18, p. 4861.
32. Balcells, D., Maseras, F., and Khiar, N., *Org. Lett.,* 2004, vol. 6, no. 13, p. 2197.

33. Johnson, C.R. and McCants, D., Jr., *J. Am. Chem. Soc.,* 1965, vol. 87, no. 23, p. 5404.

34. Lett, R., Bory, S., Moreau, B., and Marquet, A., *Bull. Soc. Chim. Fr.,* 1973, nos. 9–10, p. 2851.

35. Ben, R.N., Breau, L., Bensimon, C., and Durst, T., *Tetrahedron.,* 1994, vol. 50, no. 20, p. 6061.

36. Chan, T.H. and Ong, B.S., *Tetrahedron Lett.,* 1976, vol. 17, no. 5, p. 319.

37. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al'-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *Gaussian,* Pittsburgh, PA: Gaussian, 2003.

38. Shainyan, B.A. and Kirpichenko S.V., *Russ. J. Gen. Chem.,* 2003, vol. 73, no. 11, p. 1709.

39. Fieser, L.F. and Fieser, M., *Reagents for Organic Synthesis,* New York: Wiley–Interscience, vol. 3, 1972. Translated under the title *Reagents for Organic Synthesis,* Moscow: Mir, 1976, vol. 3, p. 459.