^1H and ^{13}C NMR study of tin-containing sulfoxide, sulfimide, and sulfoximide

Yu. A. Kurskii,[a] N. E. Stolyarova,[a] V. I. Shcherbakov,[a] I. A. Borisova,[b] and A. N. Ponomarev[b]*

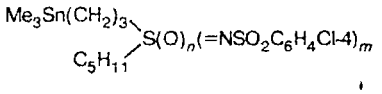
[a] *G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603600 Nizhny Novgorod, Russian Federation. Fax: 007 (831 2) 66 1497. E-mail: imoc@infotel.ru*

[b] *"Caprolactam" Co., 606010 Dzerzhinsk, Nizhny Novogorod region, Russian Federation.*

Sulfoxide $RS(O)R'$ (**1**), sulfimide $RS(=NSO_2Ar)R'$ (**2**), and sulfoximide $RS(O)(=NSO_2Ar)R'$ (**3**) ($R = Me_3Sn(CH_2)_3$, $R' = n\text{-}C_5H_{11}$, $Ar = 4\text{-}C_6H_4Cl$) were investigated by ^1H and ^{13}C NMR spectroscopy. Unlike **3**, compounds **1** and **2** have a cyclic structure due to the intramolecular donor-acceptor S→Sn interaction.

Key words: NMR spectroscopy; structure; trimethylstannyl-containing sulfoxide, sulfimide, sulfoximide.

Previously,[1] we obtained tetraalkyl organotin compounds functionalized with sulfoxide (**1**), sulfimide (**2**), or sulfoximide (**3**) groups.



1: $n = 1$, $m = 0$; **2**: $n = 0$, $m = 1$; **3**: $n = m = 1$

Their molecules contain, first, an asymmetric center at the S atom and, second, an acceptor Sn atom and donor S and O atoms capable of coordination. In this work, the stereochemistry of these compounds was studied by ^1H and ^{13}C NMR spectroscopy.

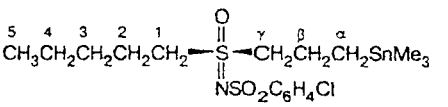
Experimental

^1H and ^{13}C NMR spectra were recorded on a Gemini-300 spectrometer (at 300 and 75 MHz, respectively) in $CDCl_3$; the concentrations of solutions for the ^1H NMR were 10—15 mg $(0.5\ mL)^{-1}$, and those for the ^{13}C NMR were 70—100 mg $(0.5\ mL)^{-1}$. A HMDS signal at δ 0.055 and a $CDCl_3$ signal at δ 77.0 were used as the internal standards for the ^1H and ^{13}C NMR, respectively. To calculate the spin-spin interaction constants from complex spectra, a program included in the standard software of the spectrometer was used. The iterative program was based on the LAME program (an advanced version of the LAOCOON program).

Compounds **1**, **2**, and **3** were synthesized by the previously described methods.[1] The molecular mass of compound **2** was determined by cryoscopic method in benzene: found 487 and 483; calculated 498.2.

Results and Discussion

Compounds containing a tri- and tetracoordinated S atom have a pyramidal and tetrahedral configuration, respectively.[2] If the sulfur atom has different substituents (as that in compounds **1**, **2**, and **3**), it becomes a chiral center. Compounds **1**—**3** studied are racemates.



The numbering used in this work for carbon atoms and the hydrogen atoms attached to them is indicated by figures and Greek letters using the sulfoximide molecule as an example.

The protons of the methylene groups bonded to the chiral center are diastereotopic, which results in their magnetic nonequivalence in the NMR spectrum.[3] Thus, the γ-CH_2 protons differ in chemical shifts in all compounds studied (Table 1). This difference is 0.098 for **1**, 0.206 for **2**, and 0.064 for **3** (in ppm units). The difference between chemical shifts of the methylene protons in position 1 is lower: 0.069 for **1**, 0.162 for **2** (also in ppm units), whereas no difference was observed for **3**. The chemical shifts of the 1-protons and those of the γ-protons were determined from the homonuclear double resonance spectra obtained with selective saturation of the signals of the 2-protons and β-protons, respectively. The $^2J(^1H—^1H)$ geminal constants at the sp^3-hybridized carbon atom and the $^3J(^1H—^1H)$ vicinal constants are known to be negative and positive, respectively.[4] The absolute values of the spin-spin coupling constants between hydrogen and tin atoms are listed in Tables 1 and 2.

The magnetic nonequivalence of diastereotopic nuclei is dependent on the character of conformational equilibria in the molecule. It can be expected that the magnetic nonequivalence decreases as the along-the-

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carbon-chain distance from the chiral center increases. However, an appreciable difference in the chemical shifts of the α-CH_2 protons is observed in compounds **1** and **2**; it amounts to 85 and 45% of the corresponding difference for the γ-CH_2 protons, respectively (Table 1). The chemical shifts of the α-CH_2 protons were also determined from the double resonance spectra. In compound **3**, the α-CH_2 protons do not differ in their chemical shifts, since a singlet is observed for them in the case of selective saturation of the β-CH_2 protons.

Table 1. Parameters of the ^{1}H NMR spectra of compounds **1**—**3**

Compound	δ	*J*/Hz	Assignment
1	0.082 s	$J(^{117}Sn) = 51.0$, $J(^{119}Sn) = 53.3$	Me_3Sn
	0.845, 0.930 (ABXX′)	$^2J_{AB} = -12.8$, $^3J_{AX} = 13.4$, $^3J_{AX'} = 3.8$, $^3J_{BX} = 4.2$, $^3J_{BX'} = 13.3$	α-CH_2Sn
	0.91 t	$^3J = 6.9$	5-Me
	1.29—1.499 m		3- и 4-CH_2
	1.75 m		2-CH_2
	1.93 m		β-CH_2
	2.621, 2.690 (ABXX′)	$^2J_{AB} = -12.4$	1-$CH_2S(O)$
	2.622, 2.720 (ABXX′)	$^2J_{AB} = -12.7$	γ-$CH_2S(O)$
2	0.048 s	$J(^{117}Sn) = 51.4$, $J(^{119}Sn) = 53.6$	Me_3Sn
	0.669, 0.761 (ABXX′)	$^2J_{AB} = -12.8$, $^3J_{AX} = 13.3$, $^3J_{AX'} = 4.5$, $^3J_{BX} = 4.2$, $^3J_{BX'} = 13.9$	α-CH_2Sn
	0.86 t	$^3J = 6.9$	5-Me
	1.18—1.35 m		3- и 4-CH_2
	1.61 m		2-CH_2
	1.71 m		β-CH_2
	2.710, 2.916 (ABXX′)	$^2J_{AB} = -12.3$	γ-$CH_2S{=}NSO_2$
	2.730, 2.891 (ABXX′)	$^3J_{AB} = -12.5$	1-$CH_2S{=}NSO_2$
	7.37—7.85 (AA′BB′)		$S{=}NSO_2C_6H_4Cl$
3	0.097 s	$J(^{117}Sn) = 51.3$, $J(^{119}Sn) = 53.7$	Me_3Sn
	0.82 (AA′XX′)	$^3J_{AX'} = 9.8$, $^3J_{AX} = 7.4$	α-CH_2Sn
	0.91 t	$^3J = 6.9$	5-Me
	1.29—1.47 m		3- и 4-CH_2
	1.83 m		2-CH_2
	1.98 m		β-CH_2
	3.34 m		1-$CH_2S(O){=}NSO_2$
	3.318, 3.382 (ABXX′)	$^2J_{AB} = -12.5$	γ-$CH_2S(O){=}NSO_2$
	7.48—7.93 (AA′BB′)		$S(O){=}NSO_2C_6H_4Cl$

Differences in the influence of the chiral center on the α-CH_2 group can be explained by intramolecular coordination in compounds **1** and **2**. It is these compounds which contain the S atom having the lone electron pair and capable of acting as an electron donor. The Sn atom exhibits electron-withdrawing properties affording its vacant pd-orbital for the donor electron pair in strong complexes and predominantly the d-orbital in weak complexes.[5] The ability of organotin compounds to be involved in the intramolecular coordination with participation of the O atom is well known. Coordination due to the donor-acceptor O→Sn interaction has been observed, for instance, in ω-(trichlorostannyl)alkylacetates $MeCO_2(CH_2)_nSnCl_3$.[6] Only the five-membered cycle is stable at $n = 3$, while the intermolecular coordination is dominant for compounds with $n = 4$ and 5.

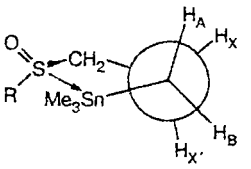
To study molecular conformations of **1**—**3**, the spin-spin coupling constants in the $SnCH_2$—CH_2 fragments were studied. The ^{1}H NMR spectra of these fragments in compounds **1** and **2** belong to the ABXX′ type, while that for compound **3** belongs to the AA′XX′ type. The ^3J vicinal constants were determined from experimental spectra by iterative calculations. The value of the $^2J_{XX'}$ geminal constant for methane (−12.4 Hz) was used in calculations.[4]

As can be seen in Table 1, the $^3J_{AX}$ constant in compounds **1** and **2** is 3.0 to 3.5 times larger than the $^3J_{AX'}$ constant, whereas the corresponding values in compound **3** differ only by a factor of 1.3. The Karplus dependence of the vicinal constant on the dihedral φ angle is described by the following equation:

$$^3J_{HH} = A + B\cos\varphi + C\cos 2\varphi. \quad (1)$$

For the carbon atom sp^3-hybridized in ethane $A = 4.22$, $B = -0.5$, and $C = 4.5$ Hz. The different sets of vicinal constants for compounds **1** and **2** as compared to that for **3** indicate that compound **3** has another conformation. In the case of free rotation about the α-C — β-C bond and equal population of hindered conformations, the ^3J constants of the spin-spin coupling between different protons of the XCH_2CH_2Y fragment differ slightly. Larger differences in the spin-spin coupling constants are observed for fixed conformations, for instance, in cyclic compounds.

In compounds **1** and **2**, the five-membered cycle can be formed due to the intramolecular S→Sn coordination. One of the conformations of **1** is shown below in the Newman projection perpendicularly to the C_α—C_β bond.

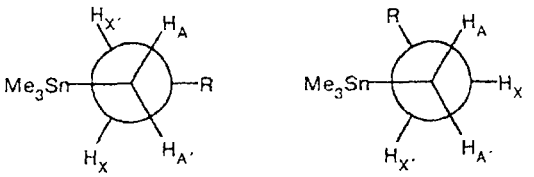


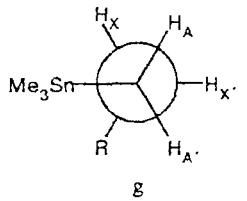
The conformation of the XCH_2CH_2Y fragment for cyclic nonaromatic systems can be reliably established using the R-factor method[8] (Eq. (2)),

$$R = \frac{^3J_{AX} + {}^3J_{BX'}}{^3J_{AX'} + {}^3J_{BX}} = \frac{3 - 2\cos^2\varphi}{4\cos^2\varphi}, \qquad (2)$$

where φ is the dihedral X—C—C—Y angle. The R-factor is defined by four vicinal constants and is independent of the electronegativity of adjacent X and Y atoms. Calculations using Eq. (2) give R-factors equal to 0.30 and 0.32 and dihedral Sn—C—C—C angles (φ) equal to 14° and 17° for compound **1** and **2**, respectively. Thus, the Sn, α-C, β-C, and γ-C atoms deviate only little from the plane of the five-membered cycles in compounds **1** and **2**.

The formation of the sterically favorable five-membered cycle in compound **3** is impossible. In this case, the small difference in the vicinal spin-spin coupling constants of the $SnCH_2—CH_2$ fragment is due to different populations of conformations.





R = $CH_2S(O)(=NSO_2C_6H_4Cl)C_5H_{11}$

Let us denote the spin-spin coupling constants for the transoid conformation as $J_{AX} = J_{A'X'} = J_t^t$ and $J_{AX'} = J_{A'X} = J_t^g$, those for the first gauche conformation as $J_{AX'} = J_g^t$, $J_{AX} = J_{A'X'} = J_g^g$, and $J_{A'X} = J_g^{g'}$, and those for the second gauche conformation as $J_{A'X} = J_g^t$, $J_{AX} = J_{A'X'} = J_g^g$, and $J_{AX'} = J_g^{g'}$. The experimentally observed constants (Table 1) are average values from the contributions of three conformations:

$$^3J_{AX} = (1 - 2p)J_t^t + 2pJ_g^g, \qquad (3)$$

$$^3J_{AX'} = (1 - 2p)J_t^g + p(J_g^{g'} + J_g^t), \qquad (4)$$

Here p is the population of one of the gauche conformations.

The vicinal constants depend not only on the dihedral angle φ, but also on the electronegativity of the substituent.[7] The replacement of H by the less electronegative Sn in an ethane-like molecule results in the increase in the ^3J spin-spin coupling constants. Therefore, it is more convenient to use the ratio of the $^3J_{AX}$ and $^3J_{AX'}$ constants ($D = {}^3J_{AX}/{}^3J_{AX'}$) rather than their values when comparing experimental and calculated constants. After simple transformations, we get the following equation from expressions (3) and (4)

$$p = \frac{J_t^t - DJ_t^g}{2(J_t^t - DJ_t^g - J_g^g) + D(J_g^g + J_g^t)}. \qquad (5)$$

Assuming that the Sn—C—C—C angle in the gauche conformations is equal to 60°, the J_t^t, J_t^g, J_g^t, J_g^g, and $J_g^{g'}$ values can be calculated from Eq. (1). Substituting them in (5), we obtain that one gauche conformation and the transoid conformation of compound **3** have populations of 26% and 48%, respectively. In accordance with this difference in populations, the potential energy of the gauche conformation of the $Me_3SnCH_2—CH_2CH_2$ fragment of compound **3** is 1.1 kJ mol^{-1} higher than that of the transoid conformation.

Participation of the Sn atom of compounds **1** and **2** in coordination interactions is confirmed by the ^{13}C NMR spectra and the $^{13}C—^{117}Sn$ and $^{13}C—^{119}Sn$ spin-spin coupling constants (Table 2). In tetraalkylstannanes, the $^1J(^{13}C—Sn)$ spin-spin coupling constants decrease in the sequence Me > Et > Pr > Bu and are equal to 340, 320, 316, and 310 Hz, respectively.[9] In the pentacoordinated tin compounds, the s-character of the Sn orbitals participating in the Sn—C bonds is a func-

Table 2. Parameters of the ^{13}C NMR spectra of compounds **1**, **2**

Compound	δ	J/Hz		Assignment
		^{13}C-^{117}Sn	^{13}C-^{119}Sn	
1	−10.5	313.1	327.9	Me_3Sn
	9.8	325.4	340.1	α-CH_2Sn
	13.6			5-Me
	20.0	14.4		β-CH_2
	22.07			2-CH_2
	22.10			4-CH_2
	30.8			3-CH_2
	52.2			1-$CH_2S(O)$
	56.4	63		γ-$CH_2S(O)$
2	−10.5	317.3	331.4	Me_3Sn
	9.0	312.1	327.3	α-CH_2Sn
	13.6			5-Me
	20.5	12.1		β-CH_2
	22.0			2-CH_2
	22.4			4-CH_2
	30.2			3-CH_2
	49.0			1-$CH_2S{=}NSO_2$
	52.5	73		γ-$CH_2S{=}NSO_2$
	127.7			*o*-CH
	128.7			*m*-CH
	137.2			—$CSO_2N{=}S$
	142.9			*p*-CCl

tion of the strength of the donor-acceptor interaction.[5] Strong complexes have a trigonal-bipyramidal configuration with a planar SnC_3 group. Hybridization of the Sn—C orbitals in the SnC_3 group is close to sp^2, and for the bonds with the fourth ligand and a donor the pd-orbitals are used. In weak complexes, the coplanarity of the SnC_3 group is violated, and hybridization of the Sn atom approaches sp^3. For compound **1**, the ^1J constant in the Me group is less than that in the α-CH_2 group. This can be explained by the decreasing contribution of the s-character of the Sn—C bond at the apical methyl group, which is not compensated by the small increase in the s-character of the equatorial groups. The increase in the ^1J constant in the CH_2 group is caused by the increasing contribution of the s-character of the equatorial Sn—α-C bond. The ^1J spin-spin coupling constants of the methyl and trimethylene groups in compound **2** differ slightly, which indicates a lower strength of the intramolecular S→Sn bond. The decrease in the temperature to −60 °C results in the decrease in the $^1J(^{13}C—^{117}Sn)$ and $^1J(^{13}C—^{119}Sn)$ constants in the Me group of compound **2** to 316.2 and 330.9 Hz, respectively. This is in agreement with the increasing portion of the complex, common for coordination interactions, as temperature decreases. Cryoscopic measurements indicate that compound **2** is monomeric in solution. Hence, in this compound, the intramolecular coordination is dominant.

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