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PREFERENTIAL CONFORMATION OF THE SIX-MEMBERED CYCLIC COMPOUNDS BEARING BOTH TRIMETHYLSILOXY(OR METHOXYMETHYLENEOXY) AND TRIBUTYLSTANNYL GROUPS AT THE GEMINAL POSITION[†]

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Abstract – The preferential conformer and conformer ratio in the cyclohexane, oxane, and thiane derivatives bearing both trimethylsiloxy (or methoxymethyleneoxy) and tributylstannyl groups at the geminal position were determined on the basis of their $^{3}J(^{119}Sn-^{13}C)$ coupling constants and ^{13}C NMR spectral analyses at low temperature.

In a series of studies on the conformational analysis of the heteroatom-substituted and six-membered cyclic compounds,[1] we have been much interested in that of compounds (**1a-c** and **2a-c**) bearing both trimethylsiloxy (TMSiO) [or methoxymethyleneoxy (MOMO)] and tributylstannyl (TBSn) groups at the geminal position. Previously, a preferential conformer in (*trans*-3-benzyloxycyclohexyl)-trimethylstannane (**3**) proved to be the Me_3Sn-equatorial (TMSn-*eq*), $PhCH_2O$-axial ($PhCH_2O$-*ax*) conformer on the basis of the ^{3}J ($^{119}Sn-^{13}C$) coupling constants (45.3 and 48.4 Hz) between C5 (or C3) and Sn of the C1-*eq* TMSn group.[2] This TMSn-*eq*, $PhCH_2O$-*ax* conformer preference should be

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[†] Dedicated to Professor Leo A. Paquette in celebration of his 70th birthday.

rationalized in terms of steric hindrance of more bulky TMSn group than $PhCH_2O$ group, which must be reasonable from the viewpoint of the *A*-values of TMSn (1.06 kcal/mol) and MeO (0.60 kcal/mol) groups calculated by Kitching *et al.*[3] McGarvey and his coworkers clearly demonstrated the axial or equatorial disposition of the TBSn group by utilizing the vicinal ^{119}Sn-C-C-^{13}C coupling constants of the rigid *tert*-butylcyclohexane derivatives such as TBSn-*eq* compound (**4**) [$^3J(^{119}Sn-^{13}C) = 40$ Hz] and TBSn-*ax* one (**5**) [$^3J(^{119}Sn-^{13}C) < 3$ Hz].[4]

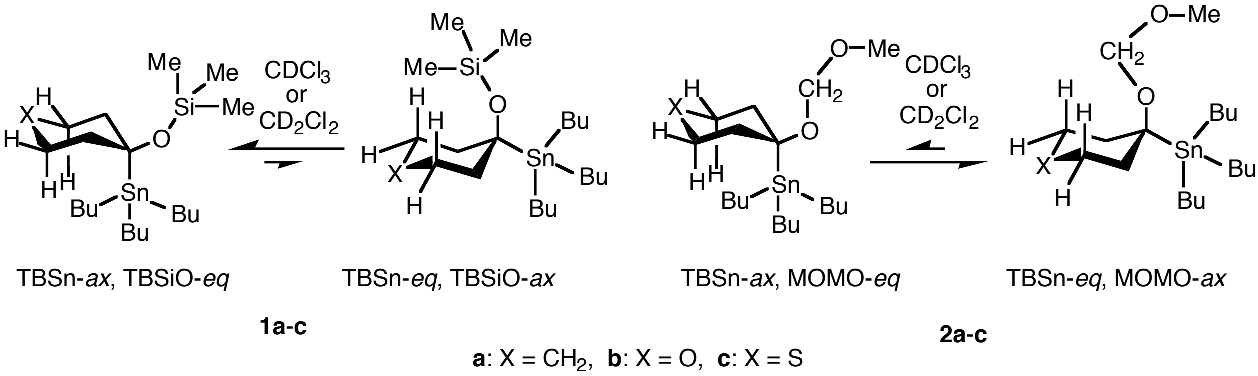


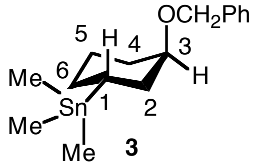
Figure 1. Conformational equilibrium mode in the cyclohexanes, oxanes, and thianes bearing both TBSn and TMSiO (or MOMO) groups at the geminal position

First of all, we determined $^3J(^{119}Sn-^{13}C)$ coupling constants of compounds (**1a-c** and **2a-c**)[5] in $CDCl_3$ at room temperature. All results including the related known data[2,4] are listed in Table 1.

Table 1. $^3J(^{119}Sn-^{13}C)$ Coupling Constants of the Organotin-Substituted Six-Membered Cyclic Compounds[a)]

Compound	$^3J(^{119}Sn-^{13}C)$ Coupling/Hz
3 [b)]	45.3 [b)], 48.4 [b)]
4 [c)]	40 [c)]
5 [c)]	< 3 [c)]
1a	7.7
1b	11.2
1c	< 11.2
2a	32.9
2b	33.6
2c	40.5

a) Determined by ^{13}C-NMR (100 MHz) spectrum in $CDCl_3$ at room temperature.
b) ref. 2 c) ref. 4



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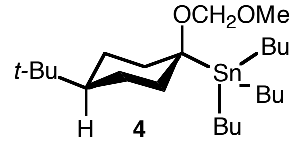

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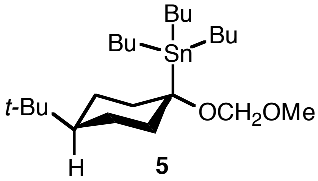

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Interestingly all ^3J values of compounds (**1a**-**c**) are smaller than 11.2 Hz, while those of compounds (**2a**-**c**) are in a range of 32.9 — 40.5 Hz.

Thus, it can be deduced that a preferential conformation in the six-membered cyclic compounds bearing a TMSiO substituent at the geminal position of the TBSn group should be TBSn-*ax* orientation, respectively. On the other hand, the six-membered cyclic compounds bearing a MOMO substituent at the geminal position of the TBSn group can predominantly adopt each corresponding TBSn-*eq* conformer.

The low-temperature ^{13}C-NMR (100 MHz, CD_2Cl_2) spectra[6] of compounds (**1a-c** and **2a,b**) gave rise to two sets of ^{13}C2,6 peaks which correspond to the TBSn-*eq* and TBSn-*ax* conformers due to their ring interconversion, as shown in Figure 1. Each conformer ratio between TBSn-*eq* conformer and TBSn-*ax* conformer and each coalescence temperature (Tc) of two sets of the peaks are recorded, as shown in Table 2. Because no two sets of ^{13}C peaks were observed on the low-temperature (CD_2Cl_2, -80 — -30 °C) spectral chart of **2c**, its conformer ratio (TBSn-*eq* : TBSn-*ax*) may be in a range of 100 : 0 — 95 : 5 on the basis of the $^{13}J(^{119}Sn-^{13}C)$ coupling constant data of **2a**-**c**. In both series of compounds (**1** and **2**), the oxane and thiane ring systems seem to affect favorably on the existence of TMSiO-*ax* and MOMO-*ax* conformers in comparison with the case of the cyclohexane ring system.

Table 2. Conformer Ratio and Coalescence Temperature between TBSn-*eq* Conformer and TBSn-*ax* one in the Six-Membered Cyclic Compounds (**1a**-**c** and **2a**,**b**) Based on the ^{13}C-NMR Spectral Analysis (100 MHz, CD_2Cl_2)[a)]

Compound	Conformer Ratio	δ(ppm) of ^{13}C2,6		Tc [b)]/ °C
	TBSn-*eq* : TBSn-*ax*	TBSn-*eq*	TBSn-*ax*	
1a	5:95	39.49	41.91	-30
1b	12:88	62.58	66.43	-45
1c	13:87	39.79	42.68	-58
2a	88:12	35.58	38.86	-45
2b	95:5	63.02	65.61	-65

a) Determined at -80 °C. b) Coalescence temp. of ^{13}C2,6 (**1a**-**c** and **2a**,**b**) peaks.

The oxane- or thiane ring effect may be rationalized by involving a possible electronic factor [σ(C3,5-H*ax*)→σ∗(C4-OMOM*ax* or C4-OSiTM*ax*) orbital overlap][1] in the molecule bearing an electron-withdrawing oxane oxygen atom or thiane sulfur atom[7] which contributes to significant stabilization of σ(C2- C3) and σ(C5- C6) orbitals in energy. In the chair-type thiane constituted of two longer C-S bonds than the corresponding C-C bond length in the cyclohexane, the usual 1,3-diaxial steric repulsion may be released a little in flexibility.

In order to explain the dramatic difference of the preferential conformer between compounds (**1a**-**c** and **2a**-**c**), we propose a main understandable term, "repulsive control between the two geminal substituents" or "buttressing effect"[8-10] on the basis of inspection of their molecular models. Namely, when compared the stability of the TBSn-*ax*, TMSiO-*eq* conformer (**A** in Figure 2) with that of the TBSn-*eq*, TMSiO-*ax* conformer (**B** in Figure 2) bearing the steric repulsion between the bulky TBSn group and the flexible TMSiO group in compounds (**1a**-**c**), the latter (**B**) must be remarkably unstable because of severe steric hindrance between the TMSi group pushed by the TBSn group and two axial protons, as shown in Figure 2. Similarly, we can compare the stability of the TBSn-*ax*, MOMO-*eq* conformer (**C** in Figure 2) with that of the TBSn-*eq*, MOMO-*ax* conformer (**D** in Figure 2) bearing the steric repulsion between the TBSn group and the flexible MOMO group in compounds (**2a**-**c**). However, the latter (**D**) is quite different from the case of the TBSn-*eq*, TMSiO-*ax* conformer (**B**) in **1a**-**c**, since more flexible and smaller MOM group than the TMSi group can be away from two axial protons, as shown in Figure 2. Hence, existence of the former (**C**) is quite little because of instability due to the steric repulsion between the TBSn group and two axial protons.

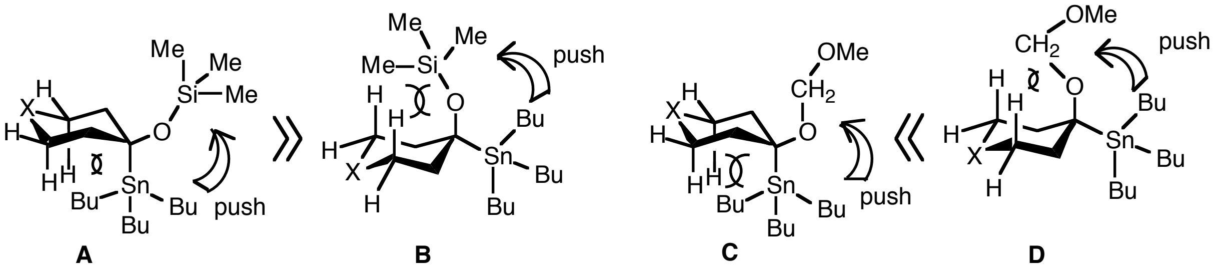

Figure 2. Sterically repulsive control between the two geminal substituents (X = CH_2, O, S)

Further, the electron-withdrawing MOMO group may cause a lowering of σ*($C4-OCH_2OMe$) in energy, which would be a little responsible for increasing the MOMO-*ax* conformer. In case of the TMSiO group, significant stabilization of σ*($C4-OSiMe_3$) can not be expected from the viewpoint of the oxygen atom basicity of the TMSiO group.[1]

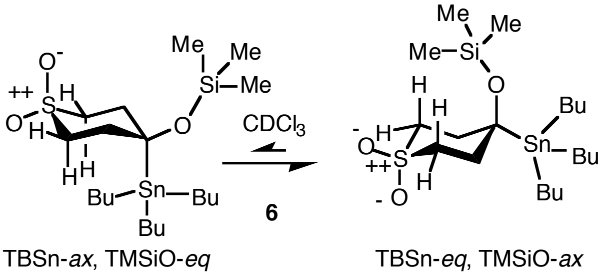

Figure 3. Conformational equilibrium mode of thiane 1,1-dioxide (**6**)

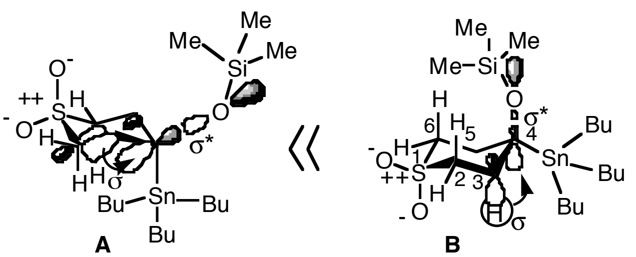

Figure 4. Stabilization of the TBSn-*eq*, TMSiO-*ax* conformation by σ(C-H)→σ*(C-OSi) orbital overlap

Surprisingly, in the sulfonic compound (**6**) (84% yield) obtained by oxidation of thiane (**1c**) with 3-chloroperbenzoic acid in CH_2Cl_2, its preferential conformer proved to be the TBSn-*eq*, TMSiO-*ax* one on the basis of $^3J(^{119}Sn-^{13}C)$ value (39.2 Hz), as shown in Figure 3.

Such a predominant existence of the TBSn-*eq*, TMSiO-*ax* conformer over the sterically favorable TBSn-*ax*, TMSiO-*eq* conformer in **6** can be explained in terms of more favorable electronic factor [σ(C3-H)$\rightarrow\sigma^*$(C4-$OSiMe_3$) orbital overlap (**B**)] than another electronic factor [σ(C2-C3)$\rightarrow\sigma^*$(C4-$OSiMe_3$) orbital overlap (**A**)], as shown in Figure 4. Because the location of the (C2-C3) orbital bond is closer to the strong electron-withdrawing sulfonyl group than that of the σ(C3-H) orbital bond, the σ(C2-C3) orbital must be more stabilized than the σ(C3-H) orbital in energy.[1]

Thus, we clarified the characteristic conformational behavior in the cyclohexanes, oxanes, and thianes bearing both TMSiO and TBSn groups or both MOMO and TBSn groups at the geminal position.

ACKNOWLEDGEMENTS

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