

Structural evidence for $\sigma_{\text{C-Sn}}-\sigma_{\text{C-O}}^*$ hyperconjugation: low temperature crystal structure of *r*-5-methyl-*c*-2-trimethylstannylcyclohexan-1-*t*-ol

Jonathan M. White* and Josie Giordano

School of Chemistry, The University of Melbourne

E-mail: j.white@oxygen.chemistry.unimelb.edu.au

Dedicated to Professor Don Cameron in recognition of his outstanding contributions to chemistry and to The University of Melbourne
(received 16 Jun 01; accepted 09 Oct 01; published on the web 17 Oct 01)

Abstract

The crystal structure of the title β -stannyl alcohol contains three molecules in the asymmetric unit. Two are anti and one is gauche. Examination of C-OH bond distances in the antiperiplanar structures provides structural evidence for $\sigma_{\text{C-Sn}}-\sigma_{\text{C-O}}^*$ hyperconjugation.

Keywords: Carbon-tin hyperconjugation, stereoelectronic effects, low temp. X-ray crystallography, solid state NMR

Introduction

The stabilisation of positive charge at the β position by group 4 metal substituents, the so-called group 4 β effect, is central to the chemistry of group 4 metal substituted organic compounds.¹⁻⁴ The most well known of these effects is the silicon β effect² which is best exemplified by the relative rates of unimolecular solvolysis of the antiperiplanar β -trimethylsilyl ester **1** which reacts 10^{12} times faster than the corresponding silicon free derivative **2**.³ The remarkable rate enhancement of **1** suggests stabilisation of the intermediate β -silyl carbenium ion **3** of ca. 18 kcal/mol. The diminished reactivity of the gauche β -silylester **4** (10^4 rel. to **2**) is consistent with the mechanism of stabilisation being hyperconjugation between the C-Si σ bonding orbital

and the carbenium p orbital.³ It has been demonstrated that stannyl and germlyl substituents have an even greater stabilising effect on positive charge at the β position.⁵ For example the trimethylgermyl ester **5** and the trimethylstannyl ester **6** react at rates 10^{14} and $\gg 10^{14}$ times faster than the corresponding metal free analogs. The C-M (M = Si, Ge, Sn) are particularly effective at stabilising positive charge by hyperconjugation for two reasons: the C-M (M = Si, Ge, Sn) σ bonds are high energy orbitals, resulting in a good energy match with the vacant carbenium ion orbital, and secondly, the C-M bonds are polarised towards the carbon, which results in particularly effective overlap with the adjacent p orbital. The ability of group IV substituents to stabilise positive charge at the β position increases down the group: Si < Ge << Sn. This trend might be expected to be related to the ionisation potentials of the C-M bonds (M = Si, Ge, Sn), these have been determined from photoelectron spectroscopy for the Et₄M compounds⁶ to be 10.04, 9.7, 8.7 e.v. resp. suggesting that a C-Si bond has similar donor properties to an oxygen non bonded pair⁷ whereas a C-Sn bond is similar to a nitrogen lone pair,⁸ and the C-Ge bonds is a slightly stronger donor than silicon. It has been demonstrated using low temperature x-ray crystallography that the presence of a trimethylsilyl or trimethylgermyl substituent antiperiplanar to a substituent at the β position results in lengthening and hence weakening of the C(alkyl)-O(ester) bond distance in the ground state.^{4,9-11} For example the C-O bond lengths in the 2,4-dinitrobenzenesulfonate esters **7** and **8** are 1.490(2) and 1.492(2) Å resp. which are significantly lengthened w.r.t the corresponding unsubstituted analog **9** which has a C-O distance of 1.476(2).¹¹ The origin of the C-O bond lengthening was proposed to be the result of a hyperconjugative like σ - σ^* interaction between the C-Si(Ge) bonding orbital and the C-O antibonding orbital (Figure 1), this interaction is close to optimum in the structures **7** and **8**. The strength of the $\sigma_{C-M} - \sigma_{C-O}^*$ interaction will depend largely on the energy difference between the σ_{C-M} orbital and the σ_{C-O}^* antibonding orbital,¹² while silicon and germanium have similar ground state effects,^{11,13} a trimethylstannyl substituent is expected to have a much larger effects. We have attempted to synthesize ester derivatives derived from the trimethylstannyl alcohols **10** and **11**¹¹ in order to investigate the structural effects of $\sigma_{C-Sn} - \sigma_{C-O}^*$ hyperconjugation, however these attempts have been thwarted by the facile elimination of the ester and trimethylstannyl substituents, even the *p*-nitrophenoxy derivatives of **10** and **11** has proved too reactive to isolate and crystallise. Thus structural evidence for $\sigma_{C-Sn} - \sigma_{C-O}^*$ interactions has thus far been elusive.

Results and Discussion

The alcohol **10** was isolated as an oil, but was found to crystallise slowly over a period of 6 months at 5° C. The x-ray structure of a rod-like crystal of **10** was determined at 130 K and is shown in Figure 2, **10** was found to exist in the solid state as three independent molecules in the asymmetric unit. Strikingly, two of the molecules (molecule one and molecule two) have the antiperiplanar conformation **10a** while molecule three exists in the gauche conformation **10b** (Table 1). The presence of two molecules of with the antiperiplanar conformation **10a** and one molecule with the conformation **10b** is also evident in the solid state nmr of **10** (Figure 3). The relevant features of the solid state nmr spectrum include the signals at -7.6 and -8.10 p.p.m which integrate to 2:1 for the Me₃Sn carbons. Both the relative integrals and the relative chemical shift values are consistent with the presence of two axial Me₃Sn substituents (δ -7.6) and one equatorial Me₃Sn substituent at higher field (δ -8.10).¹⁴ Splitting is also clearly resolved for the C1 carbon where signals at δ 70.5 and 610.2 p.p.m appear in the ratio 2:1. Interestingly the relative proportions of the antiperiplanar **10a** and gauche conformations **10b** observed in the solid state is similar to that observed in solution, thus at -100° C the ¹³C spectrum resolves into two sets of signals corresponding to **10a** and **10b** in the ratio 3:1. Molecular mechanics¹⁵ calculations which were performed on the two conformations **10a** and **10b** predict that the gauche conformation **10b** is of lower energy on steric grounds (relative energies: **10b** 0.0 kcal/mol **10a** 0.510 kcal/mol). The observation that the anti conformation **10a** predominates in solution is consistent with the presence of stabilising $\sigma_{C-Sn}-\sigma^*_{C-O}$ hyperconjugation which is maximised in the anti conformation **10a** but is expected to be negligible in the gauche conformation **10b**, this interaction is not accounted for by the molecular mechanics calculations. Structural evidence for this interaction is provided by comparing the C₁-O₁ bond distances for the three molecules (Table 1). Molecules one and two which exist in the antiperiplanar conformation **10a** have C-O bond distances 1.451 and 1.452 Å resp. which while being essentially identical with each other appear to be lengthened w.r.t molecule three which exists in the gauche conformation **10b** for which the corresponding C-O distance is 1.436(10). The C-O distance observed for **10b** is typical for a secondary alcohol which is not influenced by any special electronic effects.¹⁶ Although the $\sigma_{C-Sn}-\sigma^*_{C-O}$ interaction might be expected to result in lengthening of the C2-Sn distances of molecules in the antiperiplanar conformation **10a** relative to the gauche conformation **10b**, examination of Table 1 shows no significant differences between the three molecules. This is consistent with our observations on

silicon containing analogues in which structural effects on the C-Si bond are much smaller than those on the C-O bond distance.^{4,9-11} It is interesting to note however that the Sn-Me bonds are shorter in molecules **1** and **2** than in molecule three which suggests participation of the group SnMe₃ orbitals in the interaction.

Tentative structural evidence is therefore provided for the first time for the presence of $\sigma_{\text{C-Sn}}-\sigma^*_{\text{C-O}}$ hyperconjugation, which has been previously observed for silicon and germanium. The strength of the $\sigma_{\text{C-M}}-\sigma^*_{\text{C-O}}$ interaction depends on the energy difference between the donor orbital ($\sigma_{\text{C-M}}$) and the acceptor orbital ($\sigma^*_{\text{C-O}}$). Given that a C-Si bond has a similar energy to an oxygen lone pair orbital and that the $\sigma_{\text{C-Si}}-\sigma^*_{\text{C-O}}$ interaction results in similar structural effects as the $n_{\text{O}}-\sigma^*_{\text{C-O}}$ interaction,^{4,10} it is interesting to compare the structural effects of the $\sigma_{\text{C-Sn}}-\sigma^*_{\text{C-O}}$ interaction present in **10b** with the corresponding $n_{\text{N}}-\sigma^*_{\text{C-O}}$ interaction, e.g as might occur in **12**. An examination of the Cambridge Crystallographic Database showed only one structure which is suitable for comparison; the heterocyclic derivative **13**. The molecule exists in a conformation which allows significant overlap between the nitrogen lone pair orbital and the $\sigma^*_{\text{C-O}}$ orbital, the C-O bond distance is 1.460 Å, suggesting that the $n_{\text{N}}-\sigma^*_{\text{C-O}}$ interaction results in structural effects of a similar order of magnitude to the $\sigma_{\text{C-Sn}}-\sigma^*_{\text{C-O}}$ interaction.

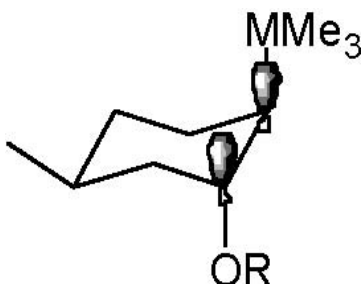
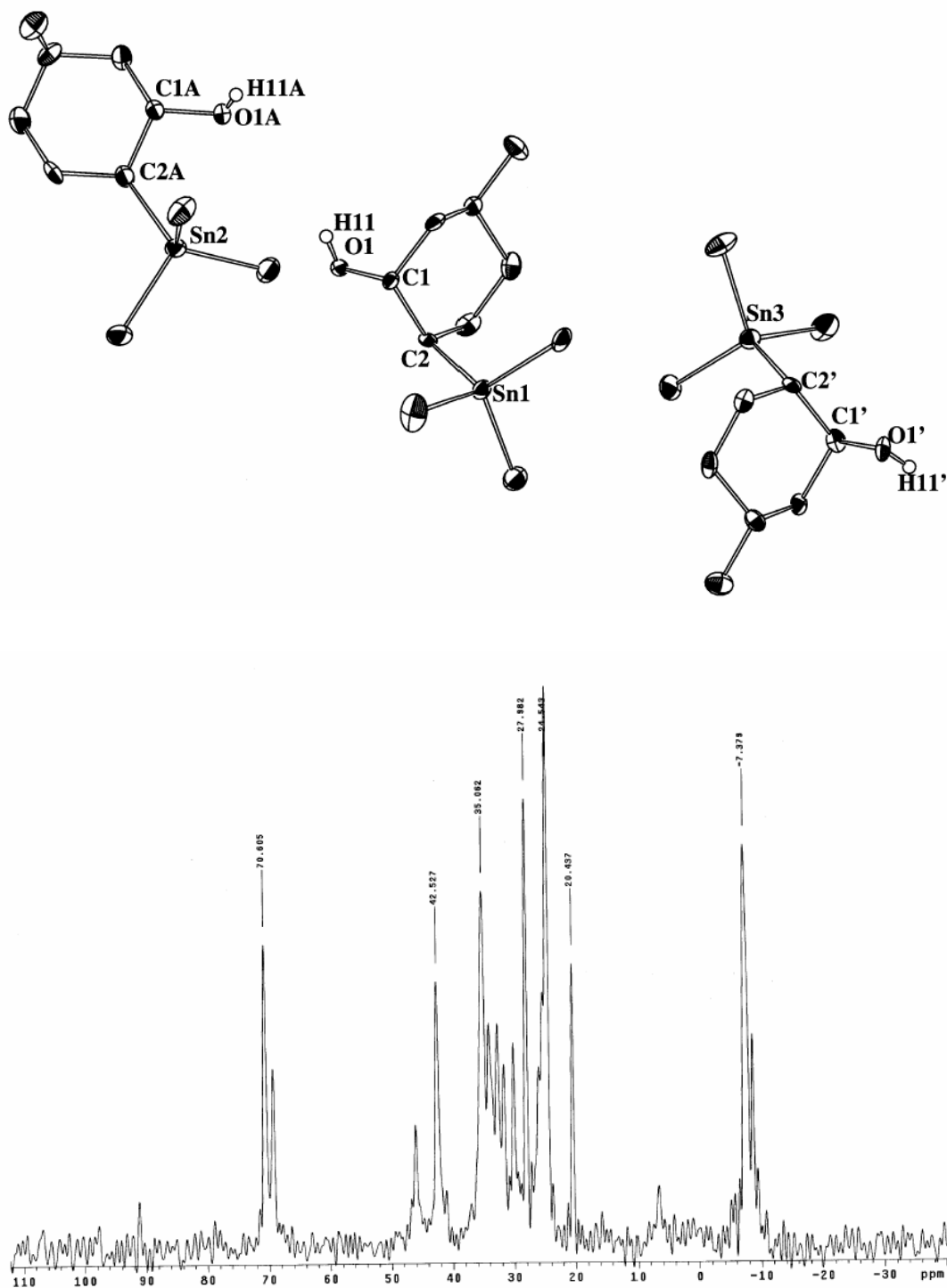
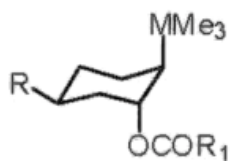
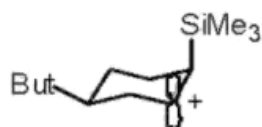
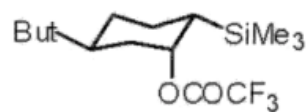
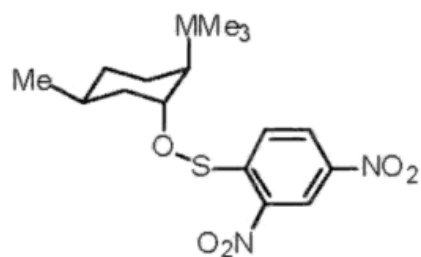


Figure 1

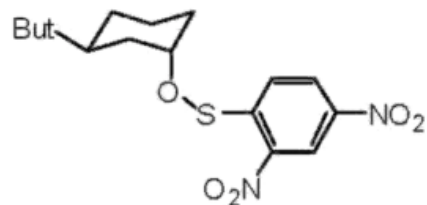
**Figure 3**

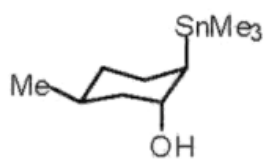
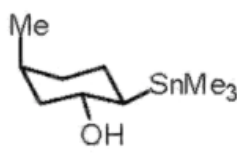
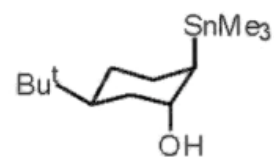
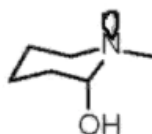
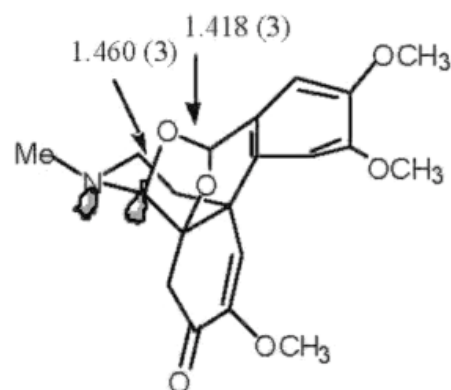


- 1**: $M = Si$, $R_1 = CF_3$, $R = Bu^t$
5: $M = Ge$, $R_1 = CF_3$, $R = H$
6: $M = Sn$, $R_1 = CH_3$, $R = Bu^t$

**2****3****4**

- 7**: $M = Si$
8: $M = Ge$

**9**

**10a****10b****11****12****13****Table 1.** Selected Structural parameters for **10**

	Molecule 1	Molecule 2	Molecule 3
Sn-C2	2.168(7)	2.159(8)	2.164(9)
Sn-Me	2.136	2.133	2.118
C1-O1	1.452(8)	1.451(8)	1.436(10)
C1-C2	1.541(11)	1.503(11)	1.512(11)
O-C(1)-C(2)-Sn	-157.4(5)	153.8(5)	56.1(8)

Experimental Section

General Procedures. The solid state ^{13}C n.m.r spectrum of **10** was determined on a Varian Inova 300 MHz spectrometer operating at 75 MHz, the sample was spinning at 8000 Hz. Contact time was 2 millisecond, C-H cross polarisation pulsed with 2 second repetition, 50 KHz width, 90° pulse for 1H was 4.5 microseconds.

Diffraction data were recorded on an Enraf Nonius CAD4f diffractometer in the range $2^\circ < \theta < 25^\circ$ (7512 reflections collected, 6580 independent (R_{int} 0.04)) operating in the $\theta/2\theta$ scan mode at low temperature (130.0(1) K). Data were corrected for Lorentz and polarization effects and for absorption (SHELX 76)¹⁸. Structures were solved by direct methods (SHELXS-86)¹⁹ and were refined on F^2 (SHELXL-97).²⁰ Hydrogen atoms were located from difference fourier maps and allowed to refine without restraint with isotropic thermal parameters. The crystal was maintained at 130 K using an Oxford Cryostream cooling device. The thermal ellipsoid plot of **10** was drawn using the program ZORTEP.²¹ Crystal data for **10**: $\text{C}_{10}\text{H}_{19}\text{OSn}$, $M = 273.9$, colourless rod (0.32 x 0.07 x 0.05 mm), m.p. 44-45 $^\circ$ C, orthorhombic, space group $P2_12_12_1$, $a = 6.765(1)$, $b = 22.606(3)$, $c = 24.518(4)$, $V = 3479.5(10)$, $F(000) = 1644$, $\mu(\text{MoK}\alpha) = 2.00 \text{ mm}^{-1}$, $Z = 4$, $\rho_{\text{calc}} = 1.456 \text{ Mg/m}^{-3}$. Final residuals were $R1$ 0.043 for 5169 unique reflections with $I > 2\sigma(I)$ and $wR2 = 0.0754$ (all data). Crystallographic data (excluding structure factors for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC -000000. Copies of this data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk

Acknowledgements

Thanks goes Frances Separovic for running the solid state ^{13}C n.m.r spectrum of 9, and the Australian Research Council Large Grants Scheme for funding this research.

References and Notes

1. Egorochkin, A. N. *Russ. Chem. Rev.* **1985**, *53*, 445.
2. Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
3. Lambert, J. B.; Wang, G.; Finzel, R. B. Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.
4. White, J. M. *Aust. J. Chem.* **1995**, *48*, 1227.
5. Lambert, J. B.; Wang, G.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422.
6. Schweig, A.; Weidner, U.; Manuel, G. *J. Organomet. Chem.* **1973**, *54*, 145.
7. Bock, H.; Mollere, P.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1973**, *61*, 113.
8. Worley, S. D. *Chem. Rev.* **1971**, *71*, 295.
9. White, J. M.; Robertson, G. B. *J. Org. Chem.* **1992**, *57*, 4638.
10. Green, A. J.; Kuan, Y. L.; White, J. M. *J. Org. Chem.* **1995**, *60*, 2734.
11. Chan, V. Y.; Clark, C. I.; Giordano, J. Green, A.J.; Karalis, A.; and White, J. M. *J. Org. Chem.* **1996**, *61*, 5227.
12. Albright, T. A.; Burdett, J. K.; Whangho, W. *Orbital Interactions in Chemistry*, Wiley: New York, 1985.
13. Adcock, W.; Cox, D. P.; Kitching, W. *J. Organomet. Chem.* **1977**, *133*, 393.
14. Wickham, G.; Olszowy, H. A.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 3788.
15. Molecular mechanics calculations using the MMX forcefield within PCMODEL version 4.0. Serena Software, Bloomington.
16. Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6197.
17. Ayral-Kalous tan, S.; Agosta, W. C. *J. Org. Chem.* 1981, 4880.
18. SHELX76: Sheldrick, G. M. *Program for Crystal Structure Determination*, Cambridge: England, 1976.
19. SHELXS-86: Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C.; Goddard, R.; Eds; Oxford University Press, Oxford: England, 1985; pp 175-189.
20. SHELXL-97: Sheldrick, G. M. *Program for Crystal Structure Refinement*. Univ. of Gottingen, Germany, 1993.

21. ZORTEP: Zsolnai, L. *An interactive ORTEP Program*, University of Heidelberg, Germany, 1994.