Structural evidence for $\sigma_{\text{C-Sn}} - \sigma^*_{\text{C-O}}$ hyperconjugation: low temperature crystal structure of $r$-5-methyl-$c$-2-trimethylstannylecyclohexan-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 $\beta$-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 $\sigma_{\text{C-Sn}} - \sigma^*_{\text{C-OH}}$ hyperconjugation.

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

Introduction
The stabilisation of positive charge at the $\beta$ position by group 4 metal substituents, the so-called group 4 $\beta$ 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 $\beta$ effect$^2$ which is best exemplified by the relative rates of unimolecular solvolysis of the antiperiplanar $\beta$-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 $\beta$-silyl carbenium ion $3$ of ca. 18 kcal/mol. The diminished reactivity of the gauche $\beta$-silylester $4$ ($10^4$ rel. to $2$) is consistent with the mechanism of stabilisation being hyperconjugation between the C-Si $\sigma$ bonding orbital
and the carbenium p orbital.\textsuperscript{3} It has been demonstrated that stannyl and germyl substituents have an even greater stabilising effect on positive charge at the $\beta$ position.\textsuperscript{5} For example the trimethylgermyl ester 5 and the trimethylstannyl ester 6 react at rates $10^{14}$ and $>>10^{14}$ 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) $\sigma$ 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 $\beta$ 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 Et$_4$M compounds\textsuperscript{6} 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 pair\textsuperscript{7} whereas a C-Sn bond is similar to a nitrogen lone pair,\textsuperscript{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 $\beta$ position results in lengthening and hence weakening of the C(alkyl)-O(ester) bond distance in the ground state.\textsuperscript{4,9-11} For example the C-O bond lengths in the 2,4-dinitrobenzenesulfenate 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).\textsuperscript{11} The origin of the C-O bond lengthening was proposed to be the result of a hyperconjugative like $\sigma$-$\sigma^*$ 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 $\sigma^*_{\text{C-M}}$-$\sigma_{\text{C-O}}$ interaction will depend largely on the energy difference between the $\sigma_{\text{C-M}}$ orbital and the $\sigma^*_{\text{C-O}}$ antibonding orbital,\textsuperscript{12} while silicon and germanium have similar ground state effects,\textsuperscript{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\textsuperscript{11} in order to investigate the structural effects of $\sigma^*_{\text{Sn}}$-$\sigma_{\text{C-O}}$ 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 $\sigma^*_{\text{C-Sn}}$-$\sigma_{\text{C-O}}$ 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 σC-Sn-σ* 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 σC-Sn-σ* 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. 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 $\sigma_{C-Sn}\sigma^*_{C-O}$ hyperconjugation, which has been previously observed for silicon and germanium. The strength of the $\sigma_{C-M}\sigma^*_{C-O}$ interaction depends on the energy difference between the donor orbital ($\sigma_{C-M}$) and the acceptor orbital ($\sigma^*_{C-O}$). Given that a C-Si bond has a similar energy to an oxygen lone pair orbital and that the $\sigma_{C-Si}\sigma^*_{C-O}$ interaction results in similar structural effects as the $n_O\sigma^*_{C-O}$ interaction, it is interesting to compare the structural effects of the $\sigma_{C-Sn}\sigma^*_{C-O}$ interaction present in 10b with the corresponding $n_N\sigma^*_{C-O}$ 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 $\sigma^*_{C-O}$ orbital, the C-O bond distance is 1.460 Å, suggesting that the $n_N\sigma^*_{C-O}$ interaction results in structural effects of a similar order of magnitude to the $\sigma_{C-Sn}\sigma^*_{C-O}$ interaction.

Figure 1
Figure 3
1: M = Si, R₁ = CF₃, R = Bu⁻¹
5: M = Ge, R₁ = CF₃, R = H
6: M = Sn, R₁ = CH₃, R = Bu⁻¹

3

4

7: M = Si
8: M = Ge

9
Table 1. Selected Structural parameters for 10

<table>
<thead>
<tr>
<th></th>
<th>Molecule 1</th>
<th>Molecule 2</th>
<th>Molecule 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-C2</td>
<td>2.168(7)</td>
<td>2.159(8)</td>
<td>2.164(9)</td>
</tr>
<tr>
<td>Sn-Me</td>
<td>2.136</td>
<td>2.133</td>
<td>2.118</td>
</tr>
<tr>
<td>C1-O1</td>
<td>1.452(8)</td>
<td>1.451(8)</td>
<td>1.436(10)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.541(11)</td>
<td>1.503(11)</td>
<td>1.512(11)</td>
</tr>
<tr>
<td>O-C(1)-C(2)-Sn</td>
<td>-157.4(5)</td>
<td>153.8(5)</td>
<td>56.1(8)</td>
</tr>
</tbody>
</table>
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)\textsuperscript{18}. Structures were solved by direct methods (SHELXS-86)\textsuperscript{19} and were refined on F$^2$ (SHELXL-97).\textsuperscript{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.\textsuperscript{21} Crystal data for 10: C$_{10}$H$_{19}$OSn, M = 273.9, colourless rod (0.32 x 0.07 x 0.05 mm), m.p. 44-45° C, orthorhombic, space group P2$_1$2$_1$2$_1$, a = 6.765(1), b = 22.606(3), c = 24.518(4), V = 3479.5(10), F(000) = 1644, $\mu$(MoKα) = 2.00 mm$^{-1}$, Z = 4, $\rho_{calc}$ = 1.456 Mg/m$^{-3}$. Final residuals were R1 0.043 for 5169 unique reflections with I > 2σ(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

15. Molecular mechanics calculations using the MMX forcefield within PCMODEL version 4.0. Serena Software, Bloomington.