

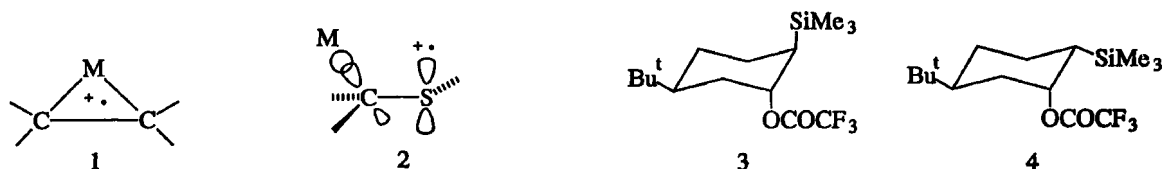
Sulfur cation radicals

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Abstract: The oxidation potentials of 2-silylated and 2-stannylated 1,3-dithianes have been determined by cyclic voltammetry. There is substantial, geometry-dependent, lowering of the oxidation potential by tin substituents as illustrated by 2,2-bis(trimethylstannyl)-1,3-dithiane whose oxidation potential of 0.19V is almost 1V lower than that of 1,3-dithiane itself. The UV He I photoelectron spectrum of this compound shows that its two lowest ionization potentials of 7.48 and 7.97 eV are about 1 eV lower than those of 1,3-dithiane. X-ray crystallographic structure studies on 2,2-bis(trimethylstannyl)-1,3-dithiane reveal that it adopts a chair conformation with an axial and an equatorial tin substituent. Variable temperature ^{13}C NMR spectroscopic studies demonstrate that this compound undergoes ring inversion in solution with a barrier of approximately 13.5 kcal/mol.

Aliphatic sulfur cation radicals, R_2S^+ , are novel reactive intermediates that are formed on one-electron oxidation of dialkyl thioethers. The factors that control such electron-transfer and the stability of the sulfur cation radicals obtained are of interest. Metals and metalloids adjacent to the sulfur atom of thioethers may facilitate electron-transfer from the thioether and stabilize the sulfur cation radical obtained. This stabilization may result from bridging as shown in **1**, hyperconjugation between the carbon-metal σ -bond and sulfur p-orbital as shown in **2** which requires the interacting bond and orbital to be coplanar, or inductive effects.



The interaction between a carbon-metal bond and sulfur cation radical may be analogous to that between carbenium ions and adjacent carbon-metal bonds. Experimental studies show that dramatic geometry-dependent interaction between an adjacent carbon-silicon bond and carbocationic center. Thus, the relative rates of solvolysis of **3**, **4**, and cyclohexyl trifluoroacetate in 97% aqueous trifluoroethanol are $2 \times 10^{12} : 4 \times 10^4 : 1$ (1). Theoretical studies show that the large rate acceleration of **3** is due to stabilization of the carbocationic center by Si-C hyperconjugation (2). The antiperiplanar geometry of **3** provides greater stabilization than the synclinal geometry of **4**. Stabilization of carbocationic centers by an adjacent C-Sn bond is even greater than that observed with C-Si bonds (3). In contrast to the substantial stabilization of carbenium ions by an adjacent C-Si bond, interaction between carbon radicals and adjacent C-Si bond is modest.

The electrochemical oxidation potential of ethers in acetonitrile is rendered less anodic by at least 0.9V by an adjacent C-Si bond (4). *Ab initio* calculations suggest that hyperconjugative stabilization of the oxygen cation radical by the adjacent C-Si σ -bond contributes to facilitated oxidation but is not the major factor responsible for this result. The major factor is the geometry-dependent destabilization of the ether lone pair HOMO by the adjacent C-Si σ -bond. That is, the energy of the HOMO of the ether is raised by overlap of the filled 2p-orbital of the oxygen atom with the filled C-Si σ -bond. Despite the substantial effect of an adjacent C-Si σ -bond on the oxidation potential of ethers, the effect on thioethers is modest at best. The interaction of a carbon-metal σ -bond and heteroatom p-orbital depends on their energies. The closer they are in energy the greater their interaction. Since the ionization potential of a C-Si σ -bond, 9.5–10.6 eV (5), is close to that of an ether oxygen lone pair,

TABLE 1. Peak potentials for the oxidation of 2-substituted 1,3-dithianes **5** determined by cyclic voltammetry

R	R'	Ep ^a	R	R'	Ep ^a	R	R'	Ep ^a
H	H	1.18 ^b	Me ₃ Si	Ph	0.85	Me ₃ Sn	H	0.74 ^d
Me ₃ Si	H	0.99	Me ₃ Si	Me ₃ Si	0.70	Me ₃ Sn	Bu ^t	0.55
Et ₃ Si	H	0.95	Me ₃ Si	Me ₃ Sn	0.44 ^d	Bu ₃ Sn	Bu ^t	0.54
Me ₂ Bu ^t Si	H	1.02 ^c	Et ₃ Si	Me ₃ Sn	0.38 ^d	Me ₃ Sn	Ph	0.79 ^d
Pr ₃ Si	H	0.81	Pr ₃ Si	Me ₃ Sn	0.35 ^d	Bu ₃ Sn	Ph	0.86 ^d
Me ₃ Si	Bu ^t	0.95	Me ₂ Bu ^t Si	Me ₃ Sn	0.35 ^d	Me ₃ Sn	Me ₃ Sn	0.19

^aPeak potential at Pt electrode in acetonitrile, 0.1M LiClO₄, versus 0.1M AgNO₃/Ag electrode, at a scan rate of 100 mV/s

^bLiterature value (8)

^cShoulder at 0.93 V

^dProblems with adsorption overcome by setting the initial potential just below the peak potential and scanning as soon as the electrode was placed in the sample.

The effect on the oxidation potential of 1,3-dithiane by metallation at C2 may be compared with alkylation at this position. The oxidation potentials of 2-alkyl and 2-aryl-1,3-dithianes are 0.73-0.75V and a second such substituent has no significant further effect on the oxidation potential (13). Thus an equatorial alkyl or aryl substituent lowers the oxidation potential of 1,3-dithiane but an additional axial substituent is without further effect. The oxidation potentials of C2 metallated 1,3-dithianes are in the range of 0.74-1.02 V as seen in Table 1. The effect of a 2-trimethylstannyl group is comparable to that of a 2-alkyl or aryl group in lowering the oxidation potential but curiously the effect of a 2-silyl substituent is more modest. In contrast to the comparable effects of an equatorial stannyl substituent and alkyl or aryl groups, an axial tin substituent substantially lowers the oxidation potential of 1,3-dithiane. This is most dramatically illustrated by **5**, R=R'=Me₃Sn whose peak potential of 0.19 V is almost 1 V less positive than that of 1,3-dithiane itself. The effect of an axial stannyl group is also evident in the 2-silyl-2-stannyl and 2-t-butyl-2-stannyl derivatives but ameliorated by conformational equilibria. In the case of **5**, R=R'=Me₃Sn, there must be an axial tin substituent if the molecule adopts a chair conformation. Ring inversion of the chair forms interconverts axial and equatorial tin substituents in this case. On the other hand, 2-silyl-2-stannyl and 2-t-butyl-2-stannyl-1,3-dithianes each have two interconverting chair conformations: one with the stannyl group axial and the other with this substituent equatorial. Another factor which may contribute to the exceptional lowering of the

TABLE 2. Peak potentials for the oxidation of anancomeric 1,3-dithianes determined by cyclic voltammetry

Compound	Ep ^a
6a	1.12
6b	1.13
6c	0.75 ^b
6d	0.40 ^{b,c}
6e	0.34

^aPeak potential at Pt electrode in acetonitrile, 0.1M LiClO₄, versus 0.1M AgNO₃/Ag reference electrode, at a scan rate of 100 mV/s.

^bProblems with adsorption overcome by setting the initial potential just below the peak potential and scanning as soon as the electrode was placed in the sample.

^cPeak potential at a glassy carbon electrode was 0.29V and the adsorption problem diminished.

TABLE 3. Comparison of ¹³C NMR spectra of **5**, R=R'=Me₃Sn at 190 K and **6e** at room temperature

Parameter	5 , R=R'=Me ₃ Sn	6e
δ(ax Me ₃ Sn) ^a	-9.67	-8.56
δ(eq Me ₃ Sn) ^a	-5.78	-4.83
δC(2) ^a	19.75	29.68 ^c
δC(4,6) ^a	29.50	39.87 ^d
δC(5) ^a	25.33	44.35 ^e
³ J[ax Sn-C(4,6)] ^b	14.7	14.5
³ J[eq Sn-C(4,6)] ^b	37.5	39.9

^aChemical shift values in ppm versus Me₄Si

^bCoupling constants in Hz

^cδ of 21.15 ppm is calculated when 19.75 is corrected for C4,6 Me effect

^dδ of 38.90 ppm is calculated when 29.50 is corrected for C4,6 Me effect

^eδ of 43.33 ppm is calculated when 25.33 is corrected for the C4,6 Me effect

oxidation potential of **5**, $R=R'=Me_3Sn$ is that the two vicinal tin substituents may interact with each other lowering the C-Sn ionization potential. Such interaction between geminal Me_3Sn substituents in $(Me_3Sn)_2CHCH_3$ has been reported (14). The lowered C-Sn ionization potential in **5**, $R=R'=Me_3Sn$ results in a better energy match between this bond and sulfur 3p-lone pair resulting in greater interaction, raising of the HOMO energy, and lowering of the oxidation potential. An axial silyl substituent also lowers the oxidation potential of 1,3-dithiane as illustrated by **5**, $R=R'=Me_3Si$ but the effect is small compared with that of an axial tin substituent. The greater effect of an axial tin substituent than that of an equatorial tin substituent appears to be illustrated by the lower oxidation potential of **6d** than **6c** as seen in Table 2. If both **6c** and **6d** adopt chair conformations then the tin substituent in **6c** is equatorial and that in **6d** is axial. The substantially lower oxidation potential for **6d** compared with **6c** is consistent with greater interaction between the C-Sn bond and sulfur lone pair when the tin substituent is axial than equatorial. However, the predominant conformation of **6d** in solution is not a chair as shown below by NMR spectroscopic studies.

Photoelectron Spectroscopy

The exceptionally low oxidation potential of **5**, $R=R'=Me_3Sn$ prompted determination of its ionization potential by photoelectron spectroscopy. The photoelectron spectrum of 1,3-dithiane has been reported (15). The ionization potentials of 8.54 and 8.95 eV are ascribed to removal of sulfur 3p-nonbonding electrons. There are two such ionization potentials due to the interaction of the p-type lone pair orbitals on each of the two sulfur atoms. The photoelectron spectrum of **5**, $R=R'=Me_3Sn$ is shown in Fig. 1. The lowest ionization potentials are 7.48 and 7.97 eV. Thus the ionization potentials for **5**, $R=R'=Me_3Sn$ are about 1 eV lower than those for 1,3-dithiane itself. Both the photoelectron spectroscopic ionization potentials and electrochemical peak potential demonstrate the remarkable facilitation of electron-transfer from **5**, $R=R'=Me_3Sn$ compared with 1,3-dithiane.

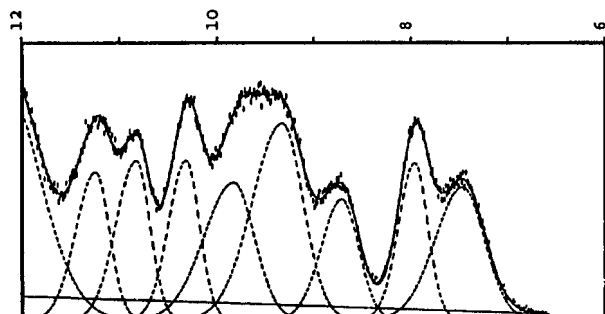


Fig. 1 UV He I photoelectron spectrum of **5**, $R=R'=Me_3Sn$. Dotted lines represent curve fitting of the experimental spectrum.

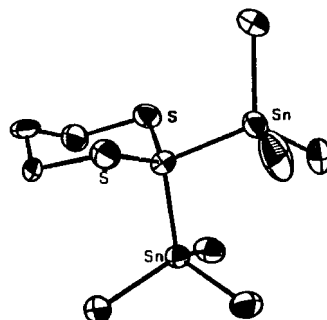


Fig. 2 ORTEP Drawing of **5**, $R=R'=Me_3Sn$. Thermal ellipsoids are drawn at the 50% probability level.

X-Ray Crystallography

The conformation of **5**, $R=R'=Me_3Sn$ in the solid state was unequivocally determined by X-ray crystallographic techniques. The molecule crystallizes in the monoclinic space group $P2_1/c$ with $a=13.1084(5)\text{\AA}$, $b=16.456(1)\text{\AA}$, $c=15.394(7)\text{\AA}$, and $\beta=93.320(4)^\circ$. An ORTEP drawing of the molecule is shown in Fig. 2. The bond lengths and bond angles are within the expected ranges and the molecule adopts a chair conformation.

NMR Spectroscopy

Insight into the conformational behavior of **5**, $R=R'=Me_3Sn$ in solution was obtained by variable temperature ^{13}C NMR spectroscopic studies in CD_2Cl_2 . At room temperature only one absorption was measured for the carbon atoms of the Me_3Sn groups at -6.73 ppm. However, on cooling this signal broadened and then separated into two signals of equal intensity at -9.67 [$^1J(^{13}C-^{119,117}Sn)=344,328\text{ Hz}$] and -5.78 ppm [$^1J(^{13}C-^{119,117}Sn)=305,290\text{ Hz}$] at 190 K as shown in Fig. 3. From the coalescence temperature of *ca.* 242 K a barrier for ring inversion of 13.5 kcal/mol was calculated. This barrier is significantly higher than that of 10.3 kcal/mol reported for chair-chair interconversion of 2,2-dimethyl-1,3-dithiane (16). In contrast to the dynamic behavior of **5**, $R=R'=Me_3Sn$, **5**, $R=Me_3Sn$, $R'=H$ does not undergo ring inversion and the tin substituent remains equatorially disposed (17). It has also been

reported that the magnitude of $^3J(^{13}\text{C}-^{119,117}\text{Sn})$ depends on the dihedral angle. For **5**, $\text{R}=\text{Me}_3\text{Sn}$, $\text{R}'=\text{H}$, with an equatorial Me_3Sn , the coupling constant between C(4,6) and equatorial tin is 37.5 Hz and that between C(4,6) and axial tin is 14.7 Hz.

Variable temperature ^{13}C NMR spectroscopic studies on **5**, $\text{R}=\text{Et}_3\text{Si}$, $\text{R}'=\text{Me}_3\text{Sn}$ in CD_2Cl_2 reveal ring inversion. One absorption for the Me_3Sn group is observed at room temperature but at 190 K two signals are seen at -8.23 and -4.53 ppm in a 3:2 ratio. The presence of the conformer with an axial Me_3Sn groups accounts for the substantial lowering of the oxidation potential for the 2-silyl-2-stannyl-1,3-dithianes reported in Table 1. A similar explanation applies to the lowered oxidation potential of 2-*t*-butyl-2-stannyl-1,3-dithianes. The lack of a lowered oxidation potential for 2-phenyl-2-stannyl-1,3-dithianes is a reflection of the known preference for an equatorial tin substituent in **5**, $\text{R}=\text{Ph}$, $\text{R}'=\text{Me}_3\text{Sn}$ (**17**).

As shown in Table 3, the ^{13}C NMR spectrum of **6e** at room temperature is very similar to that of **5**, $\text{R}=\text{R}'=\text{Me}_3\text{Sn}$ at 190 K when the chemical shift data are corrected for the effect of the C4,6 Me groups. The ^{119}Sn NMR spectrum of **6e** also shows nonequivalent Me_3Sn groups with two absorptions at 21.93 and 25.62 ppm versus Me_4Sn . Thus **6e** adopts a static chair conformation with an axial and an equatorial Me_3Sn group. Surprisingly, the ^{13}C and ^{119}Sn chemical shift for the equatorial Me_3Sn group in **6c**, -6.96 and 15.54 ppm respectively, are very close to those for the presumed axial Me_3Sn group in **6d**, -7.63 and 15.49 ppm respectively. In contrast, the ^{13}C chemical shifts for the axial and equatorial Me_3Sn groups in **6e** differ by 3.73 ppm and their ^{119}Sn chemical shifts differ by 3.69 ppm. Furthermore, the ^{13}C chemical shifts for the axial and equatorial Me_3Sn groups in **5**, $\text{R}=\text{R}'=\text{Me}_3\text{Sn}$ at 190 K differ by 3.89 ppm. Consequently it was surmised that **6d** does not adopt a chair conformation. Indeed **6g** is suggested to adopt a boat (10) or equilibrating twist (18) conformations. Nuclear Overhauser enhancements were used to prove that the predominant conformation of **6d** is not a chair. The axial H4,6 atoms are close in space to axial H2 in the chair conformation of **6c** with an equatorial Me_3Sn group. Irradiation of H4,6 results in a 26% nOe. The axial H4,6 atoms are far removed from equatorial H2 in **6d** with an axial Me_3Sn and irradiation of H4,6 resulted in no nOe of H2. However, irradiation of H5 results in a 46% nOe of H2. In a chair conformation axial H5 and equatorial H2 are widely separated but in a boat or twist conformation these hydrogen atoms are very close to each other. This result proves that **6d** preferentially adopts a twist conformation. The lower oxidation potential of **6d** compared with **6c** as seen in Table 2 may be ascribed to greater overlap of the C-Sn σ -bond and sulfur 3p orbital in the twist conformation of **6d** than in the chair conformation of **6c** or, less likely, that a small amount of the chair conformation of **6d** is present at equilibrium and it is preferentially oxidized. Finally it is interesting to note that the oxidation potential of **6e** is significantly higher than **5**, $\text{R}=\text{R}'=\text{Me}_3\text{Sn}$, although both compounds adopt chair geometries with an axial Me_3Sn group and have geminal Me_3Sn groups. This difference is ascribed to the conformational anchoring in **6e** but rapid ring inversion in **5**, $\text{R}=\text{R}'=\text{Me}_3\text{Sn}$ and that the axial C-Sn bond in a chair conformation is not optimally aligned with the sulfur 3p orbital (the torsion angle between a perpendicular to the C2-S1-C6 plane is 18° in the X-ray crystal structure geometry of **5**, $\text{R}=\text{R}'=\text{Me}_3\text{Sn}$). Attainment of conformations with a more optimized geometry for C-Sn bond interaction with the sulfur lone pair in **5**, $\text{R}=\text{R}'=\text{Me}_3\text{Sn}$ is facile but resisted in **6e**.

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