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# Neighboring Tin Effect in the Oxidation of α-Stannyl Phenyl Vinyl Sulfides

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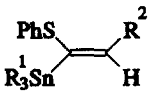
**Abstract:** α-Stannyl vinyl sulfides were generally prepared by hydrostannylation of thioacetylenes catalyzed by $Pd(PPh_3)_4$. The regio- and stereochemistry of the products was determined unequivocally in three cases by X-ray crystallographic structure studies and in the others by $^1H$ NMR spectroscopic analysis. The irreversible oxidation potentials of these compounds were determined in acetonitrile and dichloromethane by cyclic voltammetry. The oxidation potentials provide evidence for significant interaction between the C-Sn σ bond and sulfur 3p lone pair orbital in cases with appropriate geometry. © 1997 Elsevier Science Ltd.

A carbon-metal/metalloid bond adjacent to an oxygen or sulfur atom can dramatically affect its oxidation potential. Thus α-silyl,[1] germanyl,[2] and stannyl[3] ethers all have oxidation potentials less anodic than the corresponding ethers. This effect has been ascribed to a geometry-dependent raising of the HOMO energy owing to interaction between the C-M σ-bond and oxygen lone pair orbital. This interaction is greatest when the C-M σ-bond and oxygen lone pair orbital are eclipsed and least when they are orthogonal. Although the oxidation potential of α-silyl thioethers is only modestly lowered compared with the corresponding thioether,[1] there is a substantial lowering of the oxidation potential of α-stannyl thioethers as illustrated by the lowering of the oxidation potential of 1,3-dithiane of 1.18 V to 0.19V for 2,2-bis (trimethylstannyl)-1,3-dithiane.[4] The efficacy of a C-Sn over a C-Si bond in lowering the oxidation potential of thioethers is attributed to a better energy match of the sulfur 3p lone pair orbital with the C-Sn than the C-Si σ-bond and consequent greater interaction.

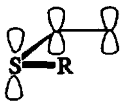
To determine if a C-Sn bond could also lower the oxidation potential of a thioether when the carbon bearing tin is $sp^2$-hybridized, a circumstance in which the lowered C-Sn bond energy is not as well-matched with the sulfur lone pair orbital, compounds **1** were prepared and studied. Calculations[5] on methyl vinyl sulfide **2** show that the energy of its HOMO, which is the 3p sulfur lone pair orbital perpendicular to the C-S-C plane, decreases slightly on rotation about the $C(sp^2)$-S bond by 90° starting from the lowest energy cis conformer **3** and resulting in conformer **4**. Further rotation results in raising its HOMO energy back to the initial energy after a further 90° rotation. In the cis conformer **3** the 3p nonbonding orbital on sulfur overlaps with the π-MO of the carbon-carbon double bond as shown. Rotation about the C-S bond by 90° renders the 3p nonbonding orbital on sulfur orthogonal to the π-MO and in the S-C-C plane as shown in **4**. In the cis conformation of **1** the 3p nonbonding orbital on sulfur is orthogonal to the C(α)-Sn bond. However, on rotation about the C-S bond by 90° to obtain the geometry of conformer **4**, these orbitals are coplanar and aligned for maximal interaction. This interaction would raise the HOMO energy and concomitantly lower the



**1a**, $R^1$ = *n*-Bu, $R^2$ = H
**b**, $R^1$ = Me, $R^2$ = H
**c**, $R^1$ = Ph, $R^2$ = H
**d**, $R^1$ = *c*-$C_6H_{11}$, $R^2$ = H
**e**, $R^1$ = *n*-Bu, $R^2$ = Me
**f**, $R^1$ = *n*-Bu, $R^2$ = Ph
**g**, $R^1$ = *n*-Bu, $R^2$ = *t*-Bu
**h**, $R^1$ = Ph, $R^2$ = *t*-Bu
**i**, $R^1$ = *c*-$C_6H_{11}$, $R^2$ = *t*-Bu
**j**, $R^1$ = *c*-$C_6H_{11}$, $R^2$ = $(c\text{-}C_6H_{11})_3Sn$
**k**, $R^1$ = *c*-$C_6H_{11}$, $R^2$ = $Me_3Si$

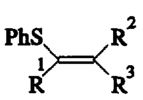
$MeSCH{=}CH_2$

**2**



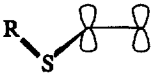
**3**

**4**

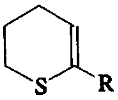


**5a**, $R^1$ = $Me_3Si$, $R^2$ = $R^3$ = H
**b**, $R^1$ = *i*-$Pr_3Si$, $R^2$ = $R^3$ = H
**c**, $R^1$ = $R^2$ = H, $R^3$ = *t*-Bu
**d**, $R^1$ = *i*-$Pr_3Si$, $R^2$ = *t*-Bu, $R^3$ = H
**e**, $R^1$ = $R^3$ = H, $R^2$ = *t*-Bu
**f**, $R^1$ = $R^3$ = H, $R^2$ = Ph
**g**, $R^1$ = $R^2$ = H, $R^3$ = Ph

lowest energy ionization potential. Consequently, such rotation about the C-S bond in **1** may lower its oxidation potential, whereas, little change or an increase in oxidation potential is expected by such rotation in vinyl sulfides in general. Furthermore, such rotation in $\alpha$-silyl vinyl sulfide **5**, $R^1 = R_3Si$ should show a modest effect at best compared with the $\alpha$-stannyl analogues **1** because interaction of C-Si $\sigma$-bond with 3p nonbonding sulfur orbitals is much less than that of C-Sn $\sigma$-bonds. Control over the conformational population of **1** may be achieved by varying the steric size of $R^2$. If $R^2 = H$ the cis conformer should be preferred. However, as the size of $R^2$ is increased gauche conformer **6** should be preferred. Although the 3p nonbonding orbital on sulfur and the C($\alpha$)-Sn orbital are not coplanar in gauche conformer **6** significant overlap and consequent interaction is expected. Compound **7a** and its $\alpha$-stannyl derivative were also prepared and studied. In this case, the cyclic system further restricts conformational mobility and these compounds serve as convenient references in which geometries comparable to **4** and **6** are precluded. The conformation of **7** is believed to be a half-chair.[6]



**6**



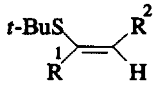
**7a**, R = H
**b**, R = $(c\text{-}C_6H_{11})_3Sn$

## RESULTS

### *Synthesis*

$\alpha$-Deprotonation of phenyl vinyl sulfide with lithium di-isopropylamide and stannylation with *n*-$Bu_3SnCl$ to give **1a** and silylation with $Me_3SiCl$ to yield **5a** has been reported.[7] Similarly, deprotonation followed by stannylation with $Me_3SnCl$, $Ph_3SnCl$, or $(c\text{-}C_6H_{11})_3$ SnCl produced **1b-d** respectively and silylation with *i*-$Pr_3SiCl$ yielded **5b**. A similar method could also be used for the stannylation of **7a**. Thus deprotonation of **7a** with *sec*-butyllithium followed by stannylation with $(c\text{-}C_6H_{11})_3SnCl$ afforded **7b**. However, a more generally useful synthesis of **1** is tin hydride addition to phenylthioalkynes **8**, $R^1$=Ph

$$R^1SC\equiv CR^2$$



**8a**, $R^1$=Ph, $R^2$=*t*-Bu; **b**, $R^1=R^2$=*t*-Bu
**c**, $R^1=R^2$=Ph; **d**, $R^1$=Ph, $R^2=(c\text{-}C_6H_{11})_3Sn$
**e**, $R^1$=*t*-Bu, $R^2=(c\text{-}C_6H_{11})_3Sn$; **f**, $R^1$=Ph, $R^2=Me_3Si$

**9a**, $R^1=(c\text{-}C_6H_{11})_3Sn$, $R^2$=*t*-Bu
**b**, $R^1=R^2=(c\text{-}C_6H_{11})_3Sn$

catalyzed by palladium (0)[8]. This reaction is regiospecific and stereospecific as shown. The Sn-H adds in a syn fashion with the tin adding to the carbon bearing sulfur. This reaction for synthesizing **1a**, **e**, **f** has been reported. In a similar way reaction of **8a** with *n*-$Bu_3SnH$, $Ph_3SnH$, and $(c\text{-}C_6H_{11})_3SnH$ gave **1g-i** respectively in satisfactory yields (67-94%). Control compound **5d** could be obtained from **1g** via the corresponding vinyllithium compound and treatment with *i*-$Pr_3SiCl$. Reaction of **8b** with $(c\text{-}C_6H_{11})_3SnH$ produced **9a** in 80% isolated yield. The requisite phenylthioalkynes could be made by the reported reaction[9] shown in eq 1 but a more convenient route to **8**, $R^1$=Ph was based on the method reported by Brandsma *et al.*[10] Deprotonation of phenylacetylene with *n*-BuLi followed by treatment with diphenyl disulfide gave **8c** in 91% isolated yield. This method could also be used to prepare **8a** on substituting *t*-butylacetylene for

$$RC\equiv CSiMe_3 + PhSSPh \xrightarrow{CuOTf} 8,\ R^1 = Ph \qquad (1)$$

phenylacetylene and similarly **8b** except that *t*-BuSTs must be used rather than *t*-BuSS*t*-Bu. Considerable difficulty was encountered in synthesizing **1j** or **9b**. Treatment of $(c\text{-}C_6H_{11})_3SnC\equiv CH$ with lithium diisopropylamide followed by PhSSPh or *t*-BuSTs afforded disproportionation products, i.e. $(c\text{-}C_6H_{11})_3SnC\equiv CSn(c\text{-}C_6H_{11})_3$ and $PhSC\equiv CSPh$ or *t*-$BuSC\equiv CS$*t*-Bu rather than **8d** or **e**. Furthermore, although **8d** or **e** could be prepared by sequential reaction of $PhSC\equiv CH$ or *t*-Bu $SC\equiv CH$, respectively, with n-butyl lithium and $(c\text{-}C_6H_{11})_3$ SnCl, the products could not be purified on silica gel chromatography owing to decomposition. Purification of the thioalkyne is essential for the catalytic hydrostannylation apparently because impurities poison the catalyst. The hydrostannylation reaction is unsuccessful with unpurified thioalkynes. Fortunately, **8d** could be purified by chromatography on deactivated alumina and hydrostannylated to yield **1j**.

### *Structure Determinations*

The conformer of lowest energy for both methyl vinyl sulfide and phenyl vinyl sulfide was found to be the cis conformer **3** by AM1 calculations.[11] However, on the basis of IR spectroscopic and dipole moment studies,[12,13] it was suggested that phenyl vinyl sulfide exists as an equilibrium mixture of two *non*-cisoidal conformers. Because of the discrepancy between the AM1 calculations and IR spectroscopic and dipole moment studies, the crystal structure of **1d** was determined. An ORTEP drawing of this molecule is shown in Fig. 1. As can be seen from this drawing, **1d** adopts the cis-conformation in the solid state. The C(phenyl-S-C(1)=C(2) torsion angle is 0.11°.

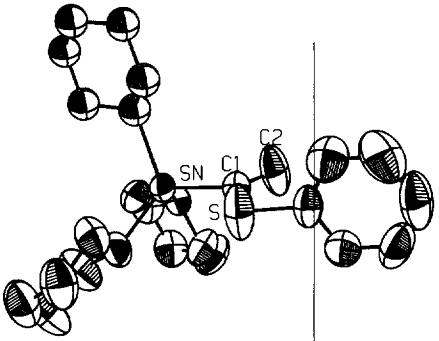


**Figure 1.** ORTEP Drawing of **1d**

The molecular structures and conformations in the solid state of **1i** and **j** were unequivocally established by single crystal X-ray structure studies. ORTEP drawings of the molecules are shown in Fig. 2 and 3, respectively. In addition to proving the regio- and stereochemistry of the tin hydride additions to the corresponding phenylthioacetylenes the structure studies show that the molecules adopt gauche conformations **6**. The C(phenyl)-S-C(1)=C(2) torsion angles are 139 and 123° for **1i** and **j** respectively.

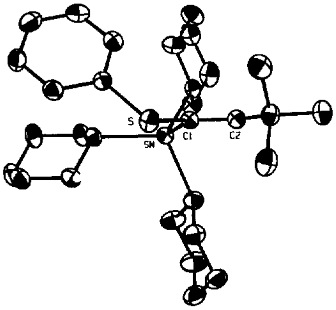


**Figure 2.** ORTEP drawing of **1i**

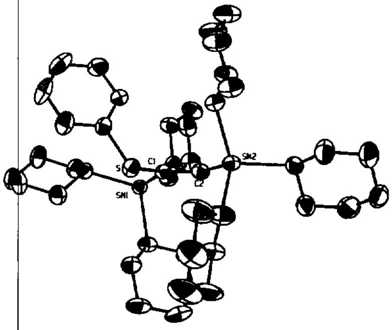


**Figure 3.** ORTEP drawing of **1j**

The structures of the other compounds **1** prepared were established by $^1H$ NMR spectroscopic analysis. The regiochemistry of the tin hydride addition to thioacetylenes addition to obtain these compounds was confirmed by the chemical shift of the vinyl hydrogen atom and the stereochemistry of the addition was determined by the $^{117,119}Sn$-$^1H$ coupling constants. These NMR parameters are listed in Table 1.

**Table 1. $^1H$ NMR Spectroscopic Parameters for Hydrostannylation Products[a]**

| Compound | $\delta_{H(vinyl)}$[b] ppm | $^3J_{Sn\text{-}H(vinyl)}$[c] Hz |
|---|---|---|
| **1e** | 6.17 | 53 |
| **1f** | 6.36 | 65 |
| **1g** | 6.03 | 54 |
| **1h** | 6.39 | 60 |
| **1i** | 6.11 | 47 |
| **1j** | 6.73 | 57 |
| **9c** | 6.07 | 50 |

[a] The spectra were measured on $CDCl_3$ solutions of the sample at 250 MHz.
[b] The chemical shifts are referenced to internal tetramethylsilane.
[c] The coupling constants reported are the average of those involving the $^{117}Sn$ and $^{119}Sn$ isotopes.

### *Oxidation Potentials*

The oxidation potentials of α-stannyl vinyl sulfides **1**, **7b**, and **9a**, phenyl vinyl sulfide, *t*-butyl vinyl sulfide and some other reference compounds **5** were determined by cyclic voltammetry in acetonitrile as well as in dichloromethane and are listed in Table 2. All of the oxidations were irreversible. The cyclic voltammograms were run at various scan rates and from the linearity of the plots of the peak current versus the square root of the scan rate the oxidations are shown to be diffusion controlled.

### *Product Study on Oxidation with Mn(III) and Ce(IV)*

Oxidation of **1g** with $Mn(OAc)_3$ in AcOH containing NaOAc gave **5c** in 41% yield on workup. Oxidation of this compound with ammonium cerium (IV) nitrate in methanol containing 2,6-di-*tert*-butylpyridine produced **5c** in 39% yield, its geometric isomer **5e** in 3% yield, and **8a** in 12% yield. The yields in these reactions were not optimized.

## DISCUSSION

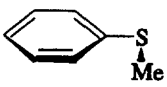
The Pd-catalyzed addition of tin hydrides to thioalkynes occurs regio- and stereospecifically to give **1** and **9a** as previously reported.[8] That is, the tin adds to the carbon bearing sulfur and the tin and hydrogen add syn to the alkyne. This is unequivocally shown by the results of the crystal structure studies of **1i** and **j**. Furthermore, $^1H$ NMR spectroscopic analysis of the other compounds **1** prepared in this study and **9a** show that they are also formed with the same regio- and stereospecificity. As shown in Table 1 the chemical shifts for the vinyl hydrogen for all of the compounds reveal that this hydrogen is attached to the vinyl carbon bearing $R^2$ not that attached to PhS for **1** or *t*-BuS for **9a**. It has been reported[14] that the three bond vicinal coupling constant between tin and hydrogen in vinyl stannanes is approximately twice as large when these nuclei are trans to each other than when they are cis. Thus, α-stannyl phenyl vinyl sulfides show two such coupling constants: **1a** (120, 55 Hz), **1b** (130, 58 Hz), **1c** (138, 63 Hz), **1d** (98, 47 Hz). The larger coupling constant (98-138 Hz) is assigned to trans Sn-H vicinal coupling and the smaller (47-63 Hz) to cis coupling. In addition, the geometry of **7b** requires the Sn and vinyl H atoms to be cis to each other and the measured Sn-H coupling constant of 47.5 Hz which is in the cis $^3J_{Sn-H}$ range further validates the use of such coupling constants to establish the stereochemistry about the double bond in α-stannylated phenyl vinyl sulfides. Since all of the vicinal Sn-H coupling constants shown in Table 1 are in the cis range the Sn and vinyl H are cis to each other in all of these compounds.

**Table 2.** **Peak Potentials for Oxidation Determined by Cyclic Voltammetry**[a]

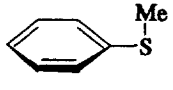
| Compound | $E_p(CH_3CN)$ | $E_p(CH_2Cl_2)$ |
|---|---|---|
| phenyl vinyl sulfide | 1.36 | 1.39 |
| *t*-butyl vinyl sulfide | 1.27 | 1.31 |
| **5f** | 0.96, 1.39 | 1.18 |
| **5g** | 0.89, 1.38 | 1.09, 1.47 |
| **5e** | 1.04, 1.38 | 1.26, 1.52 |
| **5c** | 1.01 | 1.23 |
| **5a** | 1.17 | 1.28 |
| **5b** | 1.18 | 1.21 |
| **5d** | 1.12 | 1.20 |
| **1a** | 1.13 | 1.23 |
| **1b** | 1.14 | 1.20 |
| **1c** | 1.18 | 1.26 |
| **1d** | 1.10 | 1.15, 1.27 |
| **1e** | 1.04 | 1.05, 1.32 |
| **1f** | 0.89 | 1.01 |
| **1g** | 0.87 | 1.02 |
| **1h** | 0.97 | 1.10, 1.68 |
| **1i** | 0.80 | 0.88, 1.17 |
| **1j** | 0.90 | 1.06 |
| **1k** | 0.83 | 1.00 |
| **9a** | 0.70 | 0.91 |
| **7a** | 1.03 | 1.11 |
| **7b** | 0.87 | 1.07, 1.26 |

[a]Peak potentials measured at a Pt electrode in acetonitrile solution, versus Ag/0.1 M $AgNO_3$ in acetonitrile at a 100 mV/s scan rate

AM1 calculations showed that the lowest energy conformation of phenyl vinyl sulfide is the cis-conformer **3** and the crystal structure of **1d** in which the phenyl vinyl sulfide moiety adopts a cis conformation, supports the results of these calculations. Another feature of importance revealed in this crystal structure study is the geometry about the C(phenyl)-S bond. For thioanisole there are two conformational



**10**

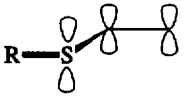


**11**

minima involving rotation about the C(phenyl)-S bond: planar conformer **10** and perpendicular conformer **11**.[15-17] In **1d** the perpendicular conformation is adopted about the C(phenyl)-S bond. It was suggested that the gauche conformer **6** would be favored by increasing the steric size of $R^2$ in **1**. The validity of this suggestion is supported by the crystal structures of **1i** and **j**. In both of these cases, the phenyl vinyl sulfide moiety adopts the gauche conformation. The conformations adopted about the C(phenyl)-S bond for these compounds is distorted planar in which approximately 36 and 31° rotation from the planar conformer for **1i** and **j**, respectively.

Consideration of the oxidation potentials shown in Table 2 provide evidence for lowering the oxidation peak potential due to interaction between the C-Sn bond and sulfur 3p-lone pair orbital. The results in dichloromethane parallel those in acetonitrile but, interestingly, are attenuated. Thus the discussion elaborated below for the results in acetonitrile apply to those in dichloromethane as well.

Interpretation of the electrochemical results is complicated because the effects observed may result from changes in HOMO energies of the phenyl vinyl sulfides, stabilization of the cation radicals obtained on one-electron oxidation or both factors. That stabilization of the cation radical is important in determining the oxidation potential is suggested by the relatively large lowering of the oxidation potential (310-470 mV) by introduction of phenyl or *t*-butyl groups β to the phenylthio moiety. If the cation radical is delocalized over the C=C π-system then substantial stabilization by the β-phenyl ring due to further delocalization and by the *t*-butyl groups by inductive and hyperconjugative effects readily account for the lowering in oxidation potentials. Such delocalization requires overlap between the sulfur p-orbital and C=C π MO. This can be achieved in the cis-conformation **3**. However, steric effects preclude this conformation in which the phenylthio moiety and bulky β-substituent are cis to each other i.e. **5e** and **f**. Nevertheless, delocalization can be achieved in the cation radicals derived from these compounds if the trans-conformer **12** is adopted.



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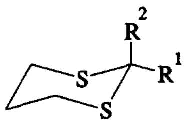


13a, $R^1 = Me_3Sn, R^2 = H$
b, $R^1 = R^2 = Me_3Sn$
c, $R^1 = R^2 = H$

Introduction of an α-*i*-$Pr_3$ Si group lowers the oxidation potential of phenylvinyl sulfide by 180 mV and an α-$Me_3Si$ group has a similar effect (190 mV lowering). This lowering in oxidation potential of a thioether due to introduction of an α-silyl substituent is similar to that observed in 1,3-dithiane. It may be ascribable to the inductive effect of a silyl group.[18] Presumably **5b** adopts cis-conformation **3** as suggested for its $\alpha$-stannyl analogue. Introduction of a $\beta$-*t*-Bu group should result in favoring gauche conformer **6**. Thus this compound **5d** should have the same geometry as **1i** and serve as an excellent model because in this $\alpha$-silyl compound the sulfur lone pair orbital can interact with the C-Si bond but with the C-Sn bond in this $\alpha$-stannyl compound. The oxidation potential of **5d** is only 60 mV lower than that of **5b** and 240 mV lower than that of phenyl vinyl sulfide. This result is important because the $\alpha$-silyl effect of 180 mV and $\beta$-*t*-butyl effect of 310 mV are *not* additive. The reason for this result may be that $\pi$-delocalization by the C=C moiety of the corresponding cation radical is mitigated because steric effects preclude adoption of either cis-conformer **3** or trans-conformer **12**. The $\beta$-*t*-butyl groups cis to the phenylthio moiety prevents adoption of conformation **3** and the $\alpha$-*i*-$Pr_3Si$ group prevents adoption of conformation **12**.

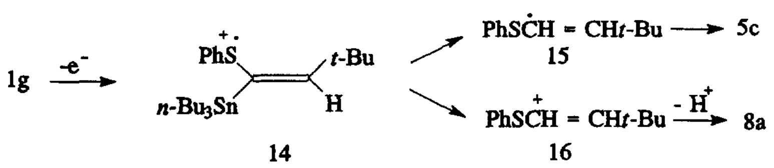
$\alpha$-Stannylation of phenyl vinyl sulfide results in a 180-260 mV drop in oxidation potential. These compounds preferentially adopt cis conformation **3**. In support of this, **1i** adopts this conformation in the solid state as seen in Fig. 1. In this conformation there is no interaction between the sulfur 3p orbital and C-Sn $\sigma$-bond because they are orthogonal. Similarly, in 2-trimethylstannyl-1,3-dithiane **13a**, in which there is little interaction between the equatorial C-Sn $\sigma$-bond and sulfur 3p orbitals, there is a comparable lowering in oxidation potential of the parent sulfide (1,3-dithiane) effected by the $\alpha$-stannyl group. Furthermore, the oxidation potential of **7a** undergoes a similar lowering of 160 mV on stannylation.[4] The conformation of **7** is geometrically restricted and precluded from becoming gauche or trans.

In compounds **1** as the steric size of the $\beta$-substituent cis to the PhS moiety increases from Me to Ph to *t*-Bu, the oxidation potentials of $\alpha$-(tri-*n*-butylstannyl) phenyl vinyl sulfides further decrease by up to 260 mV. This change in steric size of $R^3$ results in favoring gauche conformer **6** over cis conformer **3**. This change is illustrated by the gauche conformation adopted in the solid state by **1i** as seen in Fig. 2. This compound also shows a substantial lowering in oxidation potential of 300 mV compared with **1d** which adopts a cis conformation (see Fig. 1). The lowering of oxidation potentials on favoring the gauche conformation is substantially greater in the $\alpha$-stannyl compounds than the corresponding $\alpha$-silyl compounds. This suggests that the lowering of the oxidation potential is not a summation of the effects of the $\alpha$-stannyl and $\beta$-alkyl substituents but rather there is increased interaction between the sulfur lone pair orbital and C-Sn $\sigma$-bond resulting in a raising of the HOMO energy and concomitant lowering of the oxidation potential. If a $\beta$-$Me_3Si$ group is used to control the conformational geometry instead of a $\beta$-*t*-butyl group, a similar lowering in oxidation potential is observed. The observed lowering in oxidation potentials due to orbital interaction observed here (the largest of which is 560 mV compared with phenyl vinyl sulfide) are substantially lower than that observed for 2,2-bis (trimethylstannyl)-1,3-dithiane **13b** (which is almost 1V lower in oxidation potential than 1,3-dithiane **13c**).[4] The reason for this difference may be greater interaction in **13b** than gauche **1** due to (1) smaller angle between the axial C-Sn bond and sulfur 3p orbital in **13b** than the C-Sn bond and sulfur 3p orbital in gauche **1**, (2) better energy match between the C($sp^3$)-Sn $\sigma$ bond than the C($sp^2$)-Sn $\sigma$ bond and sulfur 3p orbital, (3) better energy match between HOMO resulting from combination of geminal C-Sn $\sigma$ bonds and sulfur 3p orbital.[19]

Interaction of geminal C-Sn $\sigma$ bonds has been suggested by Hosomi and Traylor[20] based on photoelectron spectroscopic studies. They also found evidence for geometry dependent interactions between vicinal C-Sn $\sigma$ bonds. Consequently, **1j** was prepared and studied. The $\beta$-stannyl substituent in these compounds controls the geometry of the phenyl vinyl sulfide moiety. As shown in Fig. 3 this compound adopts a gauche conformation. Furthermore, there may be an electronic interaction between the trans vicinal C-Sn $\sigma$-bonds which splits these orbitals and the orbital of higher energy would have greater interaction with the sulfur p-orbital because of the better energy match. However, the oxidation potential of **1j** is 100 mV *higher* than that of **1i**. The geometries of these two compounds, at least in the solid state, are comparable. Indeed there is an even smaller angle between the $\alpha$-C-Sn bond and perpendicular to the C-S-C plane in the former than the latter (20° *vs* 37°) which should result in greater interaction and concomitant lowering of oxidation potential. However, the crystal structure of **1j** reveals another factor which may account for the results. That is, the nonbonded $Sn\cdots S$ distance between the $\beta$-tin and S which are cis is 3.45 Å which is substantially shorter than the sum of their van der Waals radii (3.96 Å).[21] Consequently, there may be electron donation from S to Sn, i.e. the sulfur moiety acts as a Lewis base and the tin group acts as a Lewis acid, rendering the sulfur more difficult to oxidize. Tetraalkylstannanes are not expected to act as Lewis acids but this result may be a consequence of the unusual geometry of the system. There is scant literature precedence for such a suggestion. Transannular $Sn\cdots S$ interaction in eight-membered rings with heteroatoms attached to tin[22] and a complex of 1,5-dithiocane and tin tetrachloride have been well-characterized.[23] In addition, certain siloxanes[24-26] and an alkoxygermane[27] have been reported to function as Lewis acids.

There is an additional factor that may influence the oxidation potential of substituted phenyl vinyl sulfides. That is the conformation about the C(phenyl)-S bond. As pointed out above there are two conformational minima for thioanisole. The ionization potential for the planar conformer **10** of thioanisole is 8.02 eV and that for the perpendicular conformation is 8.55 eV.[28,29] Since, in the solid state, **1d** adopts the perpendicular conformation about the C(phenyl)- S bond but **1i** and **j** adopt conformations in which there may be phenyl $\pi$-sulfur lone pair interaction [a distorted planar conformer is adopted in which the C(phenyl)-S torsion angle is rotated by 36 and 31°, respectively, from the planar conformer], part of the difference in oxidation potential between these compounds may be due to the interaction of the phenyl $\pi$-system with the sulfur lone pair. This effect would render **1d** more difficult to oxidize than the other compounds. The magnitude of this effect is unclear, in part, because the conformations in solution are not known. Nevertheless, this effect as well as the cited interaction between the sulfur lone pair orbital and C-Sn $\sigma$-bond may be responsible for the measured differences in oxidation potential. That the interaction between the phenyl $\pi$-system and sulfur lone pair is *not* the dominant factor in determining the oxidation potentials is suggested by the modest lowering in oxidation potential of **5d** which should adopt the same geometry as **1i**. Furthermore, the difference in oxidation potential of *t*-butyl vinyl sulfide **9a** and **b** of 570 mV is comparable to that between phenyl vinyl sulfide and **1i**. Since in the *t*-butyl vinyl sulfide case the $\pi$-interaction possible in the phenyl vinyl sulfide case is precluded, it is concluded that the major factor responsible for the lowered oxidation potential of **1i** and **j** is interaction between the sulfur lone pair orbital and C-Sn $\sigma$ bond.

The oxidation products obtained by one-electron oxidation of **1g** are consistent with the formation of the corresponding sulfur cation radical **14**. $\alpha$-Stannyl thioether cation radicals are known[30-33] to undergo C-Sn



cleavage to generate the corresponding carbon radical or carbocation. Heterolysis of the $C_\alpha$-Sn bond in **14** produces carbon radical **15** which on hydrogen atom abstraction yields **5c** or its isomer **5e**. Homolysis of $C_\alpha$-

Sn bond in **14** generates carbocation **16** which on deprotonation gives **8a**. Although nucleophilic solvent could attack **16** products from such attack were not observed. Since Mn(III) oxidation yields only **5c** heterolytic fragmentation of the $C_\alpha$-Sn bond in **14** appears to be favored over homolytic fragmentation. Oxidation with Ce(IV) produces **8a** in addition to **5c** and its isomer **5e**. Although this could result from homolysis of **14** as well as heterolysis under these conditions, **16** may be formed by one-electron oxidation of **15**. Indeed Ce(IV) is known to be a better one-electron oxidant of carbon radicals than Mn(III).[34]

## EXPERIMENTAL

**General Methods.** Melting points are uncorrected. IR spectra were recorded using a Perkin-Elmer Model 983 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were measured at 250 and 62.9 MHz respectively using a Bruker AM 250 spectrometer. Mass spectra were determined using a Varian MAT 311A mass spectrometer equipped with a Varian SS-200 data system. Elemental microanalyses were done at Desert Analytics, Inc., Tucson, AZ. Commercially available chemicals from Aldrich Chemical Co., Milwaukee, WI were used as supplied unless otherwise noted. Solvents were dried using standard procedures and were made oxygen-free by the freeze-pump-thaw technique. All glassware used for anhydrous reactions was oven-dried for 12 h and allowed to cool in a desiccator. Silica gel (35-75 micron) used for column chromatography was purchased from Analtech Inc., Newark, DE.

**1-Phenylthio-1-(tricyclohexylstannyl) ethene (1d)**. The procedure reported[6] for the deprotonation of phenyl vinyl sulfide (200 mg, 1.47 mmol) was followed and tricyclohexylstannyl chloride (593 mg, 1.47 mmol) added. The reaction mixture was worked up as reported and chromatographed on silica gel to obtain a solid (547 mg, 74% yield): mp 121-122°C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.27-1.32 (m, 8H), 1.54-1.71 (m, 19H), 1.90-1.96 (m, 6H), 5.32 (s, 1H), 5.43 (s, 1H), 7.33-7.44 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 27.11, 28.16, 29.27, 32.08, 119.49, 128.01, 129.05, 132.53, 134.42, 146.42; IR (KBr) 3050, 2898, 2810, 1540, 1458, 1425, 1375, 1314, 1280, 1255, 1248, 1167, 1065, 1027, 1008, 975, 887, 874, 851, 826, 737, 706, 679, 642 $cm^{-1}$. Anal. Calcd. for $C_{26}H_{40}SSn$: C, 62.04; H, 8.01. Found: C, 62.26; H, 8.23.

**Procedure for the Preparation of 8a and 8c**. *n*-BuLi in hexanes (3.5 mL, 8.8 mmol, 2.5M) was added slowly to a solution of phenylethyne or 3,3-dimethyl-1-butyne (8.8 mmol) in anhydrous THF (10 mL) at -78°C under argon. A solution of diphenyl disulfide (1.97 g, 9.0 mmol) in anhydrous THF (8 mL) was added and the reaction mixture was stirred for 2 h at -78°C. The mixture was slowly warmed to room temperature and stirred overnight. After 12 h, the reaction mixture was poured into ice-cold saturated aqueous $NH_4Cl$ solution (30 mL), extracted with hexane (3 × 25 mL), saturated aqueous NaCl solution (1 × 30 mL), and dried (anhyd $MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure. The residue was purified by chromatography on a silica gel column eluting with hexanes to give **8c** and **8a** as colorless oils in 91 and 79% yield respectively. The $^1H$ NMR, $^{13}C$ NMR and IR spectra of the compounds prepared in this way are all identical with those obtained using the reported method.

Since **8a** is a previously unreported compound its physical characterization follows: $^1H$ NMR ($CDCl_3$) $\delta$ 1.33 (s, 9H), 7.32-7.38 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 29.04, 30.89, 63.31, 107.94, 125.43, 125.94, 129.02, 133.91; IR (neat) 3029, 3021, 2979, 2916, 2883, 2850, 1574, 1469, 1445, 1430, 1350, 1243, 1190, 1078, 1068, 1013, 987, 950, 887, 728, 679 $cm^{-1}$; MS *m/z* 190 ($M^+$), 175, 142, 121, 91, 77. Anal. Calcd. for $C_{12}H_{14}S$: C, 75.74; H, 7.42. Found: C, 75.44; H, 7.45.

**1-(t-Butylthio)-3,3-dimethyl-1-butyne (8b)**. *n*-BuLi in hexanes (0.69 mg, 1.72 mmol, 2.5 M) was added dropwise to a solution of 3,3-dimethyl-1-butyne (141 mg, 1.72 mmol) in anhydrous THF (2 mL) at -78°C under argon. The reaction mixture was stirred for 2 h at -78°C. A solution of *t*-BuSTs (428 mg, 1.75 mmol) in anhyd THF (2 mL) was added to the reaction mixture and stirred overnight. After 12 h, the reaction mixture was poured into ice-cold saturated aqueous $NH_4Cl$ solution (25 mL), extracted with hexanes (3 × 20 mL), washed with water (3 × 15 mL), saturated aqueous NaCl solution (1 × 20 mL), and dried (anhyd $MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure. The residue was purified by chromatography on a silica gel column eluting with hexanes to give **8b** (234 mg, 80% yield) as a colorless oil: $^1H$ NMR ($CDCl_3$) δ 1.26 (s, 9H), 1.39 (s, 9H); $^{13}C$ NMR ($CDCl_3$) δ 28.75, 30.00, 31.04, 46.83, 66.33, 105.41; IR (neat) 2968, 2918, 2892, 2859, 1467, 1449, 1383, 1309, 1249, 1212, 1195, 1161, 1017, 955, 928, 800 $cm^{-1}$.

**1-(t-Butylthio)-2-(tricyclohexylstannyl)ethyne (8e).** *n*-BuLi in hexanes (0.60 mL, 1.49 mmol, 2.5 M) was added dropwise to a solution of t-butylthioethyne (170 mg, 1.49 mmol) dissolved in anhyd THF (3 mL) under argon at -78°C. The reaction mixture was stirred for 2 h at -78°C. A solution of $(c\text{-}C_6H_{11})_3$ SnCl (601 mg, 1.49 mmol) dissolved in anhyd THF (3 mL) was added all at once to the mixture. The reaction mixture was stirred for 2 h, and then was slowly warmed to room temperature and stirred overnight. The mixture was then poured into ice-water, extracted with hexanes (3 × 25 mL), washed with water (3 × 15 mL) and saturated aqueous NaCl solution (1 × 20 mL), dried over anhyd $MgSO_4$ and the solvent removed by rotary evaporation under vacuum. The residue was purified by chromatography on a alumina column (neutral and deactivated to Grade III) and eluted with hexanes to give 363 mg of **8e** as a colorless solid (51% yield): mp 52-53°C; $^1H$ NMR ($CDCl_3$) δ 1.18-1.40 (m, 8H), 1.42 (s, 9H), 1.55-1.79 (m, 19H), 1.81-2.04 (m, 6H); $^{13}C$ NMR ($CDCl_3$) δ 26.89, 28.10, 28.95, 29.42, 32.03, 47.27, 96.82, 102.66; IR (KBr) 2959, 2903, 2816, 2025, 1460, 1418, 1354, 1250, 1155, 1115, 1073, 1015, 1007, 980, 899, 870. 817, 795, 653 $cm^{-1}$; MS (no molecular ion at 481) *m/z* 399, 365, 343, 261, 203, 177, 153, 121, 57. Anal. Calcd. for $C_{24}H_{42}SSn$: C, 59.89; H, 8.79. Found: C, 60.13; H, 9.00.

**General Procedure for Catalytic Hydrostannylation of Alkynes.**[7] Tetrakis (triphenylphosphine)palladium (0) (1 mole% or less) was rapidly added to a stirred solution of the 1-(phenylthio)-1-alkyne (0.8 mmol or less) dissolved in anhydrous, degassed benzene (5 mL or less) at room temperature under argon. Trisubstituted stannyl hydride (1.1 equivalent to substrate) was then added dropwise to the reaction mixture at room temperature. The reaction was over in 10-40 min. The solvent was removed by rotary evaporation under vacuum. The residue was purified by chromatography on a silica gel column eluting with hexanes to give the desired products.

**(E)-1-(Phenylthio)-1-(tri-n-butylstannyl)-3,3-dimethyl-1-butene(1g).** Starting with **8a** (95 mg, 0.50 mmol), catalytic hydrostannylation with *n*-$Bu_3SnH$ gave 225 mg (94% yield) of **1g** as a colorless oil: $^1H$ NMR ($CDCl_3$) δ 0.81-0.88 (t, 9H, $J$=7.1 Hz), 1.17-1.39 (m, 18H), 1.26 (s, 9H), 6.03 (s, 1H, Sn-H: $^3J_{cis}$=53.8 Hz), 7.11-7.16 (m, 5H); $^{13}C$ NMR ($CDCl_3$) δ 11.42, 13.64, 27.21, 28.74, 30.48, 125.73, 128.61, 129.61, 134.67, 157.95; IR (neat) 3030, 3025, 2955, 2920, 2860, 2850, 1583, 1468, 1455, 1430, 1382, 1368, 1352, 1275, 1233, 1194, 1183, 1145, 1080, 1063, 993, 953, 907, 895, 867, 856, 828, 734, 718, 685, 658 $cm^{-1}$. Anal. Calcd. for $C_{24}H_{42}SSn$: C, 59.89; H, 8.79. Found: C, 59.80; H, 8.79.

**(E)-1-(Phenylthio)-1-(triphenylstannyl)-3,3-dimethyl-1-butene(1h).** Starting with **8a** (45 mg, 0.24 mmol), catalytic hydrostannylation with $Ph_3SnH$ gave 284 mg (67% yield) of **1h** as a colorless solid: m.p. 78-79°C; $^1H$ NMR ($CDCl_3$) δ 1.32 (s, 9H), 6.39 (s, 1H, Sn-H: $^3J_{cis}$= 60.0 Hz), 6.88-7.40 (m, 20H); $^{13}C$ NMR ($CDCl_3$) δ 30.47, 36.64, 125.95, 128.24, 128.48, 128.69, 129.80, 132.78, 136.71, 137.14, 139.21, 161.71; IR (KBr) 3025, 3017, 3003, 2948, 2910, 2886, 2850, 1568, 1545, 1468, 1447, 1430, 1419, 1380, 1350, 1322, 1290, 1248, 1230, 1193, 1180, 1147, 1063, 1054, 1014, 987, 905, 896, 824, 737, 718, 688 cm$^{-1}$. Anal. Calcd. for $C_{30}H_{30}SSn$: C, 66.56; H, 5.59. Found: C, 66.41; H, 5.50.

**(E)-1-(Phenylthio)-1-(tricyclohexylstannyl)-3,3-dimethyl-1-butene (1i).** Starting with **8a** (28 mg, 0.14 mmol), catalytic hydrostannylation with $(c\text{-}C_6H_{11})_3SnH$ gave 61 mg (79% yield) of **1i** as a colorless solid: m.p. 121-122°C; $^1$H NMR ($CDCl_3$) $\delta$ 1.17-1.36 (m, 17H), 1.52-1.78 (m, 19H), 1.80-2.01 (m, 6H), 6.11 (s, 1H, Sn-H: $^3J_{cis}$=46.9 Hz), 7.25-7.27 (m, 5H): $^{13}$C NMR ($CDCl_3$) $\delta$ 27.16, 28.92, 29.34, 30.70, 32.02, 36.35, 125.26, 128.62, 128.69, 132.67, 139.17, 160.99; IR (KBr) 3020, 2900, 2835, 1458, 1460, 1347, 1243, 1154, 1065, 1027, 1010, 975, 890, 865, 825, 730, 680 cm$^{-1}$. Anal. Calcd. for $C_{30}H_{48}SSn$: C, 64.41; H, 8.45. Found: C, 64.63; H, 8.73.

**(E)-1-(Phenylthio)-1,2-bis(tricyclohexylstannyl)ethene (1j).** Starting with **8d** (127 mg, 0.25 mmol), catalytic hydrostannylation with $(c\text{-}C_6H_{11})_3$ SnH gave 178 mg (80% yield) of **1j** as a colorless solid: m.p. 133-134°C; $^1$H NMR ($CDCl_3$) $\delta$ 1.05-1.40 (m, 16H), 1.45-1.73 (m, 38H), 1.81-2.02 (m, 12H), 6.73 (s, 1H, Sn-H: $^3J_{cis}$=56.5 Hz, $^2J_{gem}$=72.7 Hz), 7.16-7.20 (m, 5H); $^{13}$C NMR ($CDCl_3$) $\delta$ 27.12, 27.21, 28.39, 29.30, 32.03, 32.36, 125.69, 128.55, 129.11; IR(KBr) 3018, 2898, 2826, 1568, 1458, 1430, 1335, 1278, 1248, 1154, 1065, 1025, 1010, 976, 892, 865, 827, 793, 725, 677, 642 cm$^{-1}$. Anal. Calcd. for $C_{44}H_{72}SSn_2$: C, 60.71; H, 8.34. Found: C, 60.72; H, 8.47.

**(E)-1-(t-Butylthio)-1-(tricyclohexylstannyl)-3,3-dimethyl-1-butene (9a).** Starting with **8b** (23 mg, 0.14 mmol), catalytic hydrostannylation with $(c\text{-}C_6H_{11})_3$ SnH gave 65 mg (88% yield) of **9c** as a colorless solid: m.p. 63-65°C; $^1$H NMR ($CDCl_3$) $\delta$ 1.20-1.42 (m, 24H), 1.57-1.81 (m, 19H), 1.89-2.04 (m, 6H), 6.07 (s, 1H, Sn-H: $^3J_{cis}$=50.0 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 27.31, 29.57, 29.74, 29.89, 31.47, 31.73, 32.19, 33.68, 131.37, 165.64; IR (KBr) 2950, 2907, 2837, 1463, 1435, 1380, 1351, 1284, 1255, 1190, 1158, 1152, 1068, 1030, 1013, 980, 898, 873, 832, 795, 733 cm$^{-1}$. Anal. Calcd. for $C_{28}H_{52}SSn$: C, 62.34; H, 9.72. Found: C, 62.18; H, 9.45.

**(E)-1-(Phenylthio)-1-(tricyclohexylstannyl)-2-(trimethylsilyl)ethene (1k).** Starting with **8f** (104 mg, 0.50 mmol) catalytic hydrostannylation with $(c\text{-}C_6H_{11})_3SnH$ gave 214 mg (75% yield) of **1k** as a colorless solid: m.p. 70-72°C; $^1$H NMR ($CDCl_3$) $\delta$ 0.21 (s, 9H), 1.03-1.31 (m, 12H), 1.31-1.51 (m, 6H), 1.53-1.81 (m, 15H), 6.44 (s, 1H, Sn-H: $^3J_{cis}$=57.4 Hz), 7.17-7.30 (m, 5H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.30, 27.14, 29.11, 29.32, 32.01, 125.84, 128.65, 129.42, 138.28, 155.67, 158.91; IR(KBr) 3018, 2920, 2828, 1488, 1463, 1434, 1235, 1157, 1072, 1013, 977, 865, 832, 730, 684, 670 cm$^{-1}$. Anal. Calcd for $C_{29}H_{48}SSiSn$: C, 60.52; H, 8.41. Found: C, 60.44; H, 8.32.

**Preparation of (E)-1-(Phenylthio)-1-(triisopropylsilyl)-3,3-dimethyl-1-butene (5d).** To a solution of **1g** (56 mg, 0.12 mmol) dissolved in anhydrous THF (2mL) containing freshly distilled HMPA (20$\mu$L) under argon and cooled to -78°C was added 2.5M *n*-BuLi in hexanes (56$\mu$L, 0.14 mmol) dropwise. After stirring for 5 h at -78°C, 2.5M triisopropylsilyl chloride in THF (0.1 mL, 0.25 mmol) was added slowly. Stirring was continued for 2 h, then the solution was allowed to warm to room temperature. After stirring overnight, the reaction was quenched by adding water (8 mL). The mixture was extracted with hexanes (3 × 15 mL). The combined organic extracts were washed with water (2 × 8 mL) and then dried (anhydr $MgSO_4$). Purification by preparative TLC on silica gel using hexanes as eluent followed by vacuum bulb-to-bulb distillation gave **5d** as a colorless oil (29 mg, 70% yield): $R_f$=0.6 (hexanes); $^1$H NMR ($CDCl_3$) $\delta$ 0.98 (d, *J*=6.6 Hz, 18H), 1.11 (m, 3H), 1.27 (s, 9H), 6.64 (s, 1H), 7.07 (m, 1H), 7.22 (d, *J*=4.3 Hz, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 11.48, 18.71, 30.63, 36.69, 124.62, 126.02, 127.56, 128.42, 139.11, 166.32; IR (neat)

2943, 2863, 1475, 1459, 882, 738, 690, 670, 643 cm$^{-1}$; MS (CI) *m/z*, 305, 255, 223, 209, 197, 177, 165, 149. Anal. Calcd for $C_{21}H_{36}SSi$: C, 72.34, H, 10.41. Found: C, 72.38, H, 9.99.

**6-(Tricyclohexylstannyl)3,4-dihydro-2H-thiin (7b).** sec-BuLi in hexanes (0.8 mL, 0.2 mmol, 2.5 M) was added slowly to a solution of **7a** (200 mg, 2 mmol) in anhyd THF (5 mL) at -78°C under argon. The mixture was stirred for 2.5 h at -78°C. Then a solution of $(c\text{-}C_6H_{11})_3SnCl$ (807 mg, 2 mmol) dissolved in anhyd THF (2 mL) was added at once to the mixture. The mixture was stirred for 3 h, then was slowly warmed to room temperature and stirred overnight. After 10 h, ice-water was added to the mixture, extracted with ethyl acetate (3 × 30 mL) and the extracts washed with water (2 × 20 mL) and saturated aqueous NaCl (1 × 20 mL), dried over anhyd $MgSO_4$ and the solvent removed by rotary evaporation under reduced pressure. The residue was purified by chromatography on a silica gel column and eluted with hexanes to give 487 mg (52% yield) of **7b** as a colorless solid: m.p. 193-196°C (d); $^1H$ NMR ($CDCl_3$) $\delta$ 1.11-1.39 (m, 10H), 1.48-1.77 (m, 17H), 1.80-2.08 (m, 8H), 2.21-2.23 (m, 2H), 2.81-2.86 (t, 2H, $J$=5.0 Hz), 5.70-5.73 (t, 1H, $J$=4.2 Hz, Sn-H: $^3J_{cis}$=47.5 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$ 22.24, 27.13, 27.51, 29.27, 32.13, 32.24, 129.11; IR (KBr) 2900, 2829, 1432, 1257, 1158, 1065, 1029, 977, 868, 830, 793, 655, 645 cm$^{-1}$. Anal. Calcd. for $C_{23}H_{40}SSn$: C, 59.11; H, 8.41. Found: C, 58.88; H, 8.41.

**Cyclic Voltammetry.** Voltammograms were measured on degassed solutions approximately $10^{-3}M$ in compound of interest and 0.1$M$ in tetra-*n*-butylammonium hexafluorophosphate in acetonitrile and in dichloromethane versus a 0.1 M Ag/0.1$M$ $AgNO_3$ in $CH_3CN$ reference electrode. A 0.3-cm$^2$ Pt flag served as the working electrode and the scan rate varied from 10-2000 mV/s. A Cyprus Systems electrochemical data system model CYSY-1 was used to acquire and process the data.

**Oxidation of 1g with $Mn(OAc)_3$.** To a solution of $Mn(OAc)_3\cdot 3H_2O$(94 mg, 0.34 mmol) and NaOAc (30 mg, 0.34 mmol) dissolved in AcOH (2 mL) and maintained at 80°C under an Ar atmosphere was added a solution of **1g** in AcOH (2 mL). After stirring 45 min the solution became colorless and was poured into ice-water, neutralized with saturated aqueous $NaHCO_3$ solution and extracted with hexanes (3 × 5 mL). The combined extracts were washed with water (3 × 5 mL) and then brine (1 × 7 mL), and dried (anhyd $MgSO_4$). The extracts were filtered and concentrated by rotary evaporation. The mixture was analyzed by $^1H$ NMR spectroscopy and quantitated by using dimethylsulfone as an internal standard. Such analysis showed **5c** formed in 41% yield.

**Oxidation of 1g with $(NH_4)_2Ce(NO_3)_6$.** To a stirring solution of **1g** (130 mg, 0.27 mmol) and 2,6-di-*tert*-butylpyridine (57 mg, 0.30 mmol) dissolved in anhyd MeOH (5 mL) under an atmosphere of Ar was added $(NH_4)_2Ce(NO_3)_6\cdot 3H_2O$ (168 mg, 0.30 mmol) all at once. The solution was stirred for 10 min and then poured into ice-water. The mixture was extracted with hexanes (3 × 5 mL) and the extracts washed sequentially with a 0.5 $M$ aqueous HCl solution (3 × 3 mL), water (3 × 5 mL) and brine (1 × 5 mL). The extracts were dried (anhyd $MgSO_4$), filtered, and concentrated using a rotary evaporator. The residue was analyzed by $^1H$ NMR spectroscopy and quantitated using dimethylsulfone as an internal standard. Such analysis revealed **5c**, **5e** and **8a** to be formed in 39, 3, and 12% yields, respectively.

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