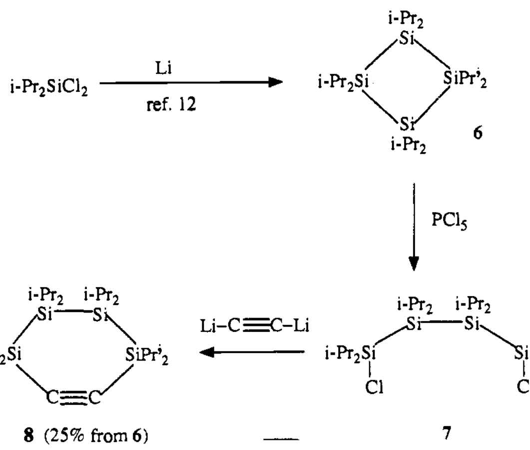
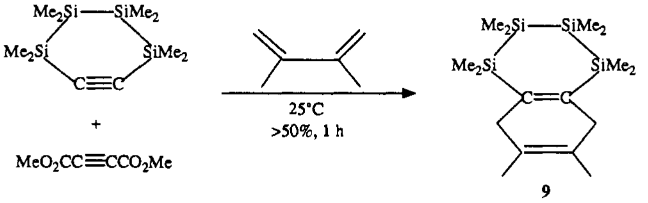
it was necessary to synthesize the more bulky derivative **8**. Synthesis of **8**[11] (colorless crystals, mp 67–68 °C) was accomplished by PCl_5-induced ring opening of cyclotetrasilane **6**[12] followed by condensation of the resulting 1,4-dichlorotetrasilane **7** with LiC≡CLi in 25% yield from **6**.



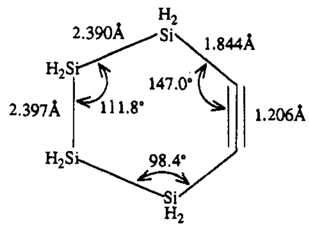
The crystal structure was solved by direct methods,[13] and the molecular structure of **8** is shown in Figure 1. Crystal packing of **8** produces a molecular asymmetry which affords Si—C≡C bond angles of 146.8° and 150.5°. The smaller bond angle of 146.8° may be compared with the C—C≡C angle of cyclooctyne,[14] 158.5°, and the smallest angle, 145.8 ± 0.7°, measured in 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne.[4]

The strain of the tetrasilacyclohexyne ring is clearly evidenced by enhanced chemical reactivity. For example, in a competition for a Diels–Alder Reaction with 2,3-dimethylbutadiene at room temperature, after 1 h, >50% of **4** had reacted to produce adduct **9**, while no detectable reaction of dimethyl acetylenedicarboxylate was observed.



The structures of tetrasilacyclohexyne (**10**) and trisilacyclopentyne (**11**) were optimized with the 6-31G(d)[15] basis set at the SCF level and verified as minima by diagonalizing the matrices of energy second derivatives (Hessians). The calculated and experimental structures for **10** agree quite well. The calculated SiCC angle of 147.0° compares well with an average experimental angle of 148.6°, although the angles in the crystal are clearly distorted by crystal packing. Ring contraction to trisilacyclopentyne (**11**) produces a dramatic reduction in the SiCC angle to 129.4°, making **11** a potentially isolable analog of benzyne.

To evaluate the stabilities of **10** and **11** the energies of the corresponding bond separation reactions[16] were determined with



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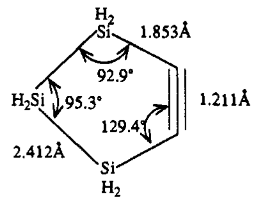

11

second-order perturbation theory (MP2)[17] and the same basis set. The bond separation reactions are

$$Si_4C_2H_8 + 2CH_4 + 4SiH_4 \rightarrow HCCH + 3SiH_3SiH_3 + 2CH_3SiH_3 \quad (1)$$

$$Si_3C_2H_6 + 2CH_4 + 3SiH_4 \rightarrow HCCH + 2SiH_3SiH_3 + 2CH_3SiH_3 \quad (2)$$

The MP2/6-31G(d) enthalpies for the isodesmic reactions 1 and 2 are respectively +18.0 and −3.1 kcal/mol. Thus any strain introduced into the acetylenic moiety by placing it into the cyclic environment of **10** is more than offset by some delocalization into the silicon backbone. The greater strain in the five-membered ring of **11** decreases this stability by more than 20 kcal/mol. Although ring contraction of silacycloalkynes by thermal extrusion of silylenes is well-known through the work of Sakurai,[18] our preliminary studies of the gas-phase pyrolysis of **4** have revealed no evidence of ring contraction to hexamethyltrisilacyclopentyne, although Me_2Si: is produced and trapped.

Acknowledgment. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. The work at Ames was supported by the Director for Energy Research, Office of Basic Energy Sciences. The theoretical study was supported by a grant from the National Science Foundation, CHE-8911911. The calculations were performed on an IBM RS6000/530 computer, purchased in part with a major instrument grant from the National Science Foundation.

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[11] **8**: mass spectrum calcd for $C_{26}H_{56}Si_4$ m/z 480.3459, found 480.3451; ^{13}C NMR (75.429 MHz, $DCCl_3$) δ 136.74 (C≡C); λ_{max}(hexane) 222 nm (log ϵ 3.51), 242 (3.41), λ_{sh} 259 (3.05). Repeated attempts failed to afford an acceptable elemental analysis. Calcd for $C_{26}H_{56}Si_4$: C, 65.01; H, 11.75. Found: C, 64.69; H, 11.49.

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Neighboring Tin Effect in Electron Transfer from Thioethers

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The neighboring silyl substituents in α-silyl ethers are known to significantly decrease the electrochemical oxidation potential of ethers,[1-3] but not thioethers.[3-5] Neighboring stannyl substituents with appropriate geometry in α-stannyl thioethers are now shown in this paper to dramatically render the anodic peak potential of the representative thioether 1,3-dithiane less positive.

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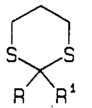
Table I. Electrochemical Oxidation Potentials for 2-Substituted 1,3-Dithianes Determined by Cyclic Voltammetry

compd	R	R^1	E_p[a]
1a	SiMe$_3$	H	0.99
1b	SiMe$_3$	tBu	0.95
1c	SiMe$_3$	Ph	0.85
1d	SiMe$_3$	SiMe$_3$	0.70
1e	SnMe$_3$	H	0.75
1f	SnMe$_3$	tBu	0.54
1g	SnMe$_3$	Ph	0.81
1h	SnMe$_3$	SnMe$_3$	0.19
1i	SiMe$_3$	SnMe$_3$	0.44

[a] Peak potentials measured at a platinum electrode in acetonitrile solution, 0.1 M LiClO$_4$, versus a Ag/0.1 M AgNO$_3$ in acetonitrile reference electrode.

It has been suggested,[3] on the basis of ab initio molecular orital calculations, that electron transfer from ethers and alcohols is facilitated in a geometry-dependent way by neighboring silyl substitution due to raising of the HOMO level in the uncharged molecule. This increase in orbital energy results from overlap between the filled oxygen 2p-orbital and the filled C–Si σ-orbital, which are comparable in energy. However, the lone pair 3p-orbital of sulfur is much lower in energy[6–8] than the C–Si σ-orbital, thereby accounting for the lack of a substantial neighboring Si effect in electron transfer from thioethers. The orbital energy of a C–Sn σ-bond[9] is close to that of a lone pair 3p-orbital on sulfur, and therefore, neighboring stannyl groups with appropriate geometry are predicted to facilitate electron transfer from thioethers. To test this prediction, we studied the oxidation of 2-(trimethylstannyl)- and 2-(trimethylsilyl)-1,3-dithianes **1** using the technique of cyclic voltammetry.[10] The results are shown in Table I. All of the oxidations were irreversible under the conditions used as is the case for 1,3-dithiane or substituted 1,3-dithianes. Alkyl or aryl groups at C(2) are known[11] to lower the electrochemical oxidation potential of 1,3-dithiane from 1.18 V to 0.73–0.75 V. As seen in Table I, a 2-trimethylsilyl substituent provides even more modest facilitation of oxidation than a 2-alkyl or -aryl group unless two such substituents are present, in which case, i.e., **1d**, the lowering is comparable. The effect of a 2-trimethylstannyl substituent, as illustrated by compounds **1e** and **1g**, is comparable to that of a 2-alkyl or -aryl group. 1,3-Dithiane has a chair conformation with an inversion barrier of 10.4 kcal/mol.[12] Metalated 1,3-dithianes strongly prefer the metal in the equatorial position[13–15] due to destabilizing carbanion lone pair/sulfur lone pair interaction in axial metal systems and stabilizing carbanion lone pair/C–S σ*-orbital interaction in equatorial metal systems according to ab initio molecular orbital calculations.[16] For these reasons the 2-trimethylstannyl group in compounds **1e** and **1g** is disposed predominantly equatorially. However, in compounds **1f** and **1i** the conformer with a 2-trimethylstannyl group in the axial position is expected to be more populated because of the 2-*tert*-butyl and 2-trimethylsilyl substituents, respectively. In compound **1h**, a trimethylstannyl group must be axial provided that the molecule adopts a chair conformation. These compounds show a dramatic lowering in oxidation potential. 2,2-Bis(trimethylstannyl)-1,3-dithiane, **1h**, has a lower peak potential than 1,3-dithiane by ca. 1 V. To ensure that the facilitated oxidation observed electrochemically was not due to some special surface effect, the photoelectron spectrum of 2,2-bis(trimethylstannyl)-1,3-dithiane was measured. The lowest ionization potentials for removal of a nonbonding electron in a 3p-orbital on a sulfur of 1,3-dithiane are lowered by ca. 1 eV in 2,2-bis(trimethylstannyl)-1,3-dithiane. Thus the neighboring tin effect is observed in a vertical ionization process in the gas phase as well.



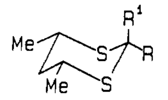
1a, R = SiMe$_3$, R^1 = H
b, R = SiMe$_3$, R^1 = tBu
c, R = SiMe$_3$, R^1 = Ph
d, R = R^1 = SiMe$_3$
e, R = SnMe$_3$, R^1 = H
f, R = SnMe$_3$, R^1 = tBu
g, R = SnMe$_3$, R^1 = Ph
h, R = R^1 = SnMe$_3$
i, R = SiMe$_3$, R^1 = SnMe$_3$

Table II. Electrochemical Oxidation Potentials for Compounds **2a–c** Determined by Cyclic Voltammetry

compd	R	R^1	E_p[a]
2a	SnMe$_3$	H	0.75[b]
2b	H	SnMe$_3$	0.40[c]
2c	SnMe$_3$	SnMe$_3$	0.35

[a] Peak potentials measured at a platinum electrode in acetonitrile solution, 0.1 M LiClO$_4$, versus a Ag/0.1 M AgNO$_3$ in acetonitrile reference electrode. [b] This peak was very broad using a platinum electrode but well-defined on glassy carbon. The oxidation potential was apparently the same with either electrode. [c] The peak potential was 0.29 V using a glassy carbon electrode.

To further elucidate the geometric dependence of the neighboring tin effect, the conformationally locked (anancomeric) 4,6-*cis*-dimethyl-1,3-dithianes **2a–c** were prepared and studied electrochemically. The peak potentials for the irreversible oxidation of these compounds obtained using cyclic voltammetry are shown in Table II, and that for the parent compound, i.e., 4,6-*cis*-dimethyl-1,3-dithiane, is 1.12 V, under the same conditions. As expected, stereoisomers **2a** and **2b** show substantially different oxidation potentials.[17] However, **1h** is substantially easier to oxidize than **2c**. The reason for this notable result may be the following. Compound **1h** but not **2c** is conformationally mobile and readily undergoes ring inversion. As suggested by the work of Yoshida et al.,[3] **1h** apparently can assume conformations not accessible to **2c** in which electron transfer is more favorable.[20]



2a, R = SnMe$_3$, R^1 = H
b, R = H, R^1 = SnMe$_3$
c, R = R^1 = SnMe$_3$

In conclusion, there is a geometry-dependent facilitation of electron transfer from thioethers by neighboring tin which results in a 1-V shift in the oxidation potential of 2,2-bis(trimethyl-

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stannyl)-1,3-dithiane, **1h**, to less positive values and a 1-eV lowering of its lowest ionization potential compared with 1,3-dithiane.[21]

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Public Health Service, National Institutes of Health, Grant No. HL15104. We thank Professor Dennis Lichtenberger and Dr. Mark Jatcho for measurement of the PES of **1h**.

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Site-Specific Adduct Formation in Oligomeric DNA Using a New Protecting Group

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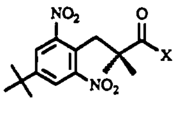
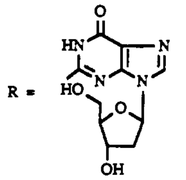
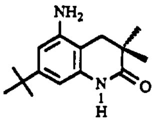
The synthesis of oligomeric DNA containing site-specifically-modified 2′-deoxynucleoside residues, which are considered to be mutagenic and/or carcinogenic lesions, is a topic of intense current interest.[1] Almost all of the methods available for such DNA syntheses involve a presynthetic strategy in which the modified base is synthesized in a protected form and then introduced into an oligomeric chain either by solution-based methods[2] or by an automated resin-based procedure.[3] Only one general *selective* postsynthetic strategy is known. This elegant method[4] involves the incorporation of a 2-fluoro-2′-deoxyinosine residue, whose fluorine atom subsequently can be replaced by treating the oligomeric DNA with an appropriate nucleophile.

We would now like to report a second approach which involves the use of a new protecting group. In this communication our strategy is demonstrated by the selective postsynthetic introduction of a single 8-fluorenylamino group into oligomers containing two 2′-deoxyguanosine residues. The protecting group that we have devised for this strategy is based on 3-(4-*tert*-butyl-2,6-dinitrophenyl)-2,2-dimethylpropionic acid (BDPDP, **1**), a compound that may be regarded as a phenyl-substituted pivalic acid. As a protecting group for the synthesis of oligomeric DNA, it carries a number of advantages: (a) it is easy to prepare,[5] (b) all three natural amino-containing 2′-deoxynucleosides implicit in DNA are easily derivatized by it,[9] (c) its amide derivatives are resistant to hydrolysis in basic solution because of its pivalate-like structure, (d) it is easily detached from the heterocyclic base by reduction[10] at neutral pH, liberating **3** by an internal ring closure reaction,[11] and lastly (e) it confers additional lipophilic character on the DNA, thus making the separation and purification of the desired 4,4-dimethoxytrityl (DMT) oligomer quite easy because it is the last peak to be eluted during chromatographic separation.



1 (X = OH) (BDPDP)
2 (X = NHR)





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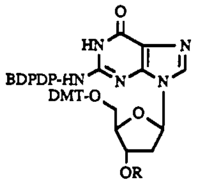

4a (R = H)
4b [R = $P(NPr^i_2)OCH_2CH_2CN$]

As a demonstration of the strategy, the BDPDP derivative of 2′-deoxyguanosine was first converted to the DMT phosphoroamidite **4b** by standard procedures.[12] This monomer was utilized with high coupling efficiency in a synthesis of two pentadecamers having compositions **5** and **6** in which dG* represents a deoxyguanosinyl residue protected by BDPDP. The other nucleosides that needed protection (dA and dG) during the synthesis were incorporated using the commercially-available phenoxyacetyl-protected forms[12c] of their DMT phosphoramidites.

5′-d(AATTG*TATAAGATAT)-3′ (**5**)

5′-d(AATTGTATAAG*ATAT)-3′ (**6**)

5′-d(AATTGTATAAGATAT)-3′ (**7**)

In the critical synthetic step, namely, the release and deprotection of the oligomer from the CPG resin support, it was found that treatment with 29% aqueous ammonia at 20 °C for 45-60 min was sufficient to remove the phenoxyacetyl groups[12c,13] while more than 80% of the BDPDP group was retained. The enhanced lipophilicity of the desired oligomers made them easy to separate,

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