

# Ground-State Stereoelectronic Effects Involving Silicon and Germanium: A Comparison of the Effects of Germanium and Silicon Substituents on C–O Bond Lengths at the $\beta$ -Position

Vee Yee Chan, Christopher I. Clark, Josy Giordano, Alison J. Green, Andrew Karalis, and Jonathan M. White\*

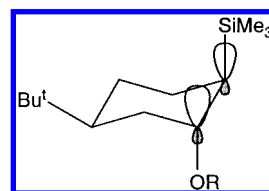
School of Chemistry, The University of Melbourne, Parkville, Victoria 3052, Australia

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Results of low-temperature crystal structures for  $\beta$ -(trimethylgermyl)-substituted cyclohexyl esters and  $\beta$ -(trimethylsilyl)-substituted cyclohexyl esters are reported. These reveal that the trimethylgermyl substituent causes significant lengthening of ester C–O bond lengths at the  $\beta$  position when compared to the corresponding unsubstituted cyclohexyl esters. Comparison of trimethylgermyl and trimethylsilyl ester C–O bond lengths suggests that the ground state effects of these two substituents are similar.

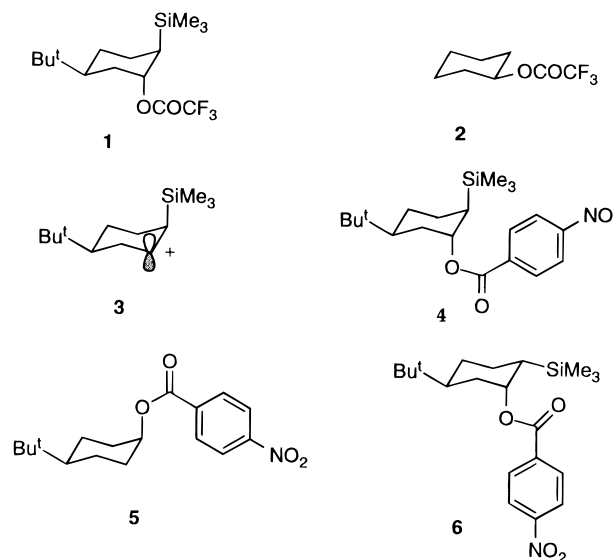
## Introduction

The stabilization of positive charge at the  $\beta$ -position is central to the chemistry of silicon-containing organic compounds.<sup>1–3</sup> This is clearly demonstrated by the enhanced rates of unimolecular solvolysis of  $\beta$ -(trimethylsilyl) esters compared to the corresponding silicon-free analogues.<sup>2,4</sup> For example, the  $\beta$ -(trimethylsilyl)-substituted trifluoroacetate ester **1** solvolyses at a remarkable  $10^{12}$  times faster than the silicon-free analogue **2**, indicating that the trimethylsilyl substituent stabilizes the intermediate cation **3** by ca. 18 kcal/mol relative to H. The origin of this remarkable stabilization is believed to be hyperconjugation between the C–Si bond and the carbocation p-orbital.<sup>1–5</sup> The C–Si bond is expected to be particularly effective at stabilizing positive charge for two reasons: it has a high energy bonding orbital, with energy (and hence donor ability) similar to that of an oxygen nonbonded pair of electrons,<sup>3</sup> and the C–Si bond is polarized toward the carbon atom (the difference in the Pauling electronegativity values for C and Si is 0.7) resulting in effective overlap with an adjacent p-orbital. We have recently demonstrated, using low-temperature X-ray crystallography, that the presence of a trimethylsilyl substituent antiperiplanar to a  $\beta$  disposed ester leaving group results in lengthening and hence weakening of the C(alkyl)–O(ester) bond in the ground state.<sup>3,6</sup> For example, the C–O bond length in the *p*-nitrobenzoate ester **4** is 1.490(2) Å, which is significantly longer than the corresponding silicon-free ester **5**, which has a C–O bond length of 1.473(2) Å. This effect is dependent upon the geometrical relationship between the trimethylsilyl and the ester group; thus, whereas **4** which has an antiperiplanar relationship between the silicon and the ester shows significant lengthening of the C–O bond, the ester **6** with a gauche relationship shows no significant C–O bond lengthening. 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 bonding



**Figure 1.**  $\sigma_{\text{C-Si}}-\sigma_{\text{C-O}}^*$  interaction between a C–Si bonding orbital and a C–O antibonding orbital in the antiperiplanar geometry.

orbital and the C–O antibonding orbital (Figure 1); this interaction is optimized in **4** where significant effects are observed but significantly reduced in **6** where overlap between the  $\sigma_{\text{C-Si}}$  and  $\sigma_{\text{C-O}}^*$  orbitals is poor.



It has been demonstrated that trimethylgermyl and trimethylstannyl substituents have even stronger stabilizing effects on positive charge at the  $\beta$  position,<sup>7</sup> with evidence to suggest that hyperconjugation is the predominant source of stabilisation. For example, the trimethylgermyl-substituted ester **7** (with corrections for population of the diaxial conformation) has been shown

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, July 1, 1996.

(1) Colvin, E. *Silicon in Organic Synthesis*; Butterworths Monographs in Chemistry; Butterworth: Boston, 1981.

(2) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(3) White, J. M. *Aust. J. Chem.* **1995**, *48*, 1227.

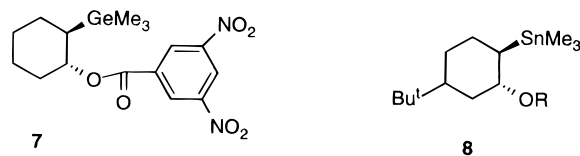
(4) Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

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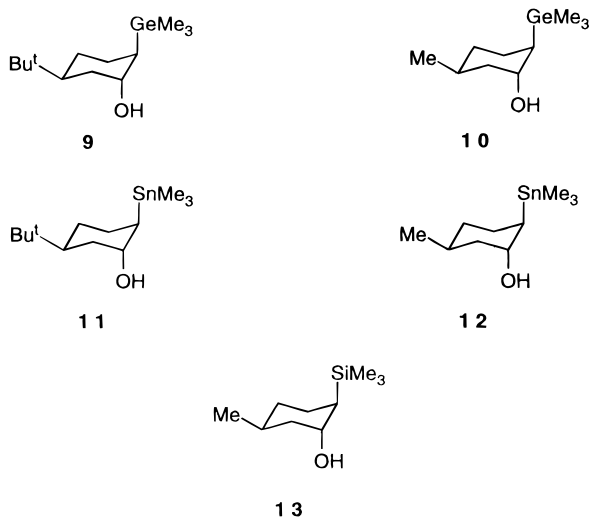
to solvolyze by a  $k_c$  mechanism at a rate  $10^{14}$  times faster than the unsubstituted ester **2**, and the trimethylstannyl esters **8** solvolyzes at  $\gg 10^{14}$  faster than **2**. The relative



rates of unimolecular solvolyses of  $\beta$ -(trimethylsilyl)-, - (trimethylgermyl)-, and - (trimethylstannyl)-substituted esters are 1,  $10^2$ , and  $\gg \text{ca. } 10^2$ , suggesting that the ability of group IV substituents to stabilize positive charge at the  $\beta$  position increases down the group:  $\text{Si} < \text{Ge} \ll \text{Sn}$ . This trend might be expected to be related to the ionization potentials of the C–M bonds ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ), which give a measure of the effectiveness of these substituents at stabilizing positive charge by hyperconjugation; these have been determined from photoelectron spectroscopy for the  $\text{Et}_4\text{M}$  compounds<sup>8</sup> to be 10.04, 9.7, and 8.7 eV, respectively, suggesting that a C–Si bond has similar donor properties to an oxygen non bonded pair,<sup>9</sup> whereas a C–Sn bond is similar to a nitrogen lone pair<sup>10</sup> and the C–Ge is somewhere in between. With the demonstrated reactivity of  $\beta$ -(trimethylgermyl) and - (trimethylstannyl) esters toward unimolecular solvolysis, we became interested in the ground state properties of these types of compounds; in particular, we were interested in determining the effects that the trimethylgermyl and trimethylstannyl substituents would have on C–O bond lengths at the  $\beta$  position and comparing these with the effects of a trimethylsilyl substituent.

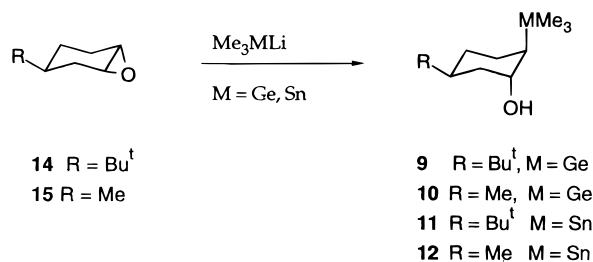
## Results

**Synthesis.** The trimethylgermyl alcohols **9** and **10**, trimethylstannyl alcohols **11**<sup>7</sup> and **12**, and the trimethylsilyl alcohol **13** were used as model substrates for the preparation of ester derivatives for X-ray analysis. The

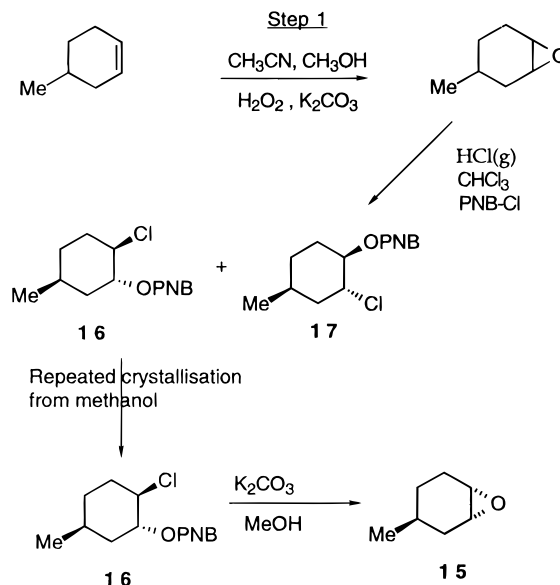


trimethylgermyl alcohol **9** and the trimethylstannyl alcohol **11** were prepared by ring opening of *trans*-4-*tert*-

## Scheme 1



## Scheme 2



butylcyclohexene oxide (**14**) with (trimethylgermyl)-lithium and (trimethylstannyl)lithium<sup>7</sup> (Scheme 1). The trimethylgermyl- and trimethylstannyl- alcohols **10** and **12** were similarly prepared by ring opening of *trans*-4-methylcyclohexene oxide (**15**) (Scheme 1). The trimethylsilyl alcohol **13** was prepared as previously described.<sup>11</sup> *trans*-4-*tert*-Butylcyclohexene oxide (**14**) was prepared by the method of Rickborn and Quartucci,<sup>12</sup> while the *trans*-4-methylcyclohexene oxide (**15**) was prepared by an analogous procedure as described in Scheme 2; 4-methylcyclohexene was converted into a ca. 1:1 mixture of *cis*- and *trans*-epoxides (step 1), which proved to be inseparable. The mixture was treated with a stream of anhydrous hydrogen chloride gas in the presence of *p*-nitrobenzoyl chloride, giving the two chloroesters **16** and **17** from diaxial epoxide ring opening. Fractional crystallization of this mixture from methanol gave the pure chloro ester **16** (10%). The chloro ester **16** was converted into the pure *trans*-epoxide **15** by treatment with potassium carbonate in refluxing methanol. The *tert*-butyl-substituted trimethylgermyl alcohol **9** was converted to the *p*-nitrobenzoate ester **18** by treatment with *p*-nitrobenzoyl chloride in pyridine, and the methyl-substituted trimethylgermyl alcohol **10** was converted into the 2,4-dinitrobenzenesulfonate ester **19** by treatment with 2,4-dinitrobenzenesulfonyl chloride in methylene chloride/pyridine. The trimethylsilyl alcohol **13** was similarly converted to the 2,4-dinitrobenzenesulfonate ester **20**. Unfortunately, all attempts to synthesize ester derivatives of the trimethylstannyl alcohols **10** and **12**

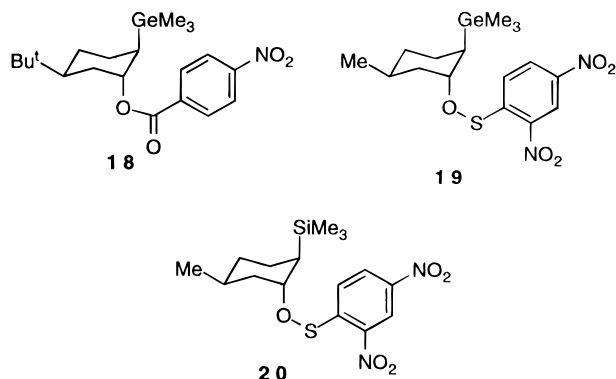
(8) Schweig, A.; Weidner, U.; Manuel, G. *J. Organomet. Chem.* **1973**, 54, 145.

(9) Bock, H.; Mollere, P.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1973**, 61, 113.

(10) Worley, S. D. *Chem. Rev.* **1971**, 71, 295.

(11) Kuan, Y. L.; White, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1195.

(12) Rickborn, B.; Quartucci, J. *J. Org. Chem.* **1964**, 29, 2476.



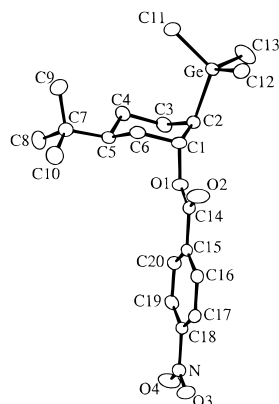
resulted in elimination of the ester and the trimethylstannyl groups giving the corresponding substituted cyclohexene; therefore, attempts to obtain accurate structural information on ester derivatives of **10** and **12** were abandoned at this point.

**Molecular Structures.** The structures of **18–20** were determined at 130 K to remove unwanted thermal effects. The structures of **18–20** and the silicon-free 2,4-dinitrobenzenesulfonate **21**, which was determined at 200 K for comparison, are presented in Figures 2–5 and were drawn using ORTEPII<sup>13</sup> to depict 50% ellipsoids. Hydrogen atoms that were refined isotropically are omitted for clarity. Selected bond lengths, angles, and dihedral angles for **18** are presented in Table 1, and selected bond lengths, angles, and dihedral angles for the sulfonate esters **19**, **20** and **21** are presented in Table 2. Atomic coordinates and thermal parameters and complete bond length and bond angle listings have been deposited with the Cambridge Crystallographic Data Centre.<sup>23</sup>

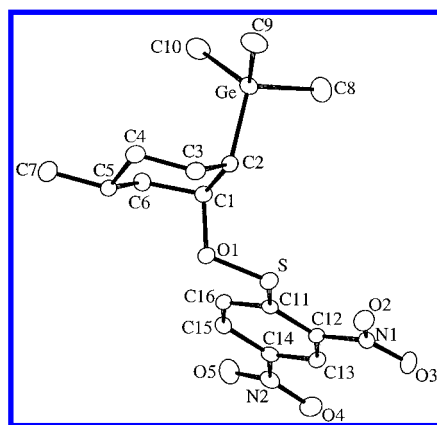
The structure of the trimethylgermyl 2,4-dinitrobenzenesulfonate **19** is isomorphous with the corresponding trimethylsilyl derivative **20**; similarly, the  $\beta$ -(trimethylgermyl)-substituted *p*-nitrobenzoate ester **18** is isomorphous with the previously reported trimethylsilyl derivative **4**.<sup>6</sup> This indicates (not surprisingly) that replacement of a trimethylsilyl substituent with the sterically similar trimethylgermyl substituent has little effect on the preferred packing in the solid state in these structures.

In structures **18–20** inspection of Tables 1 and 2 confirms the presence of angle strain at the C(1), C(2), C(3), and C(6) cyclohexane carbon centers, this manifests as a flattening of the ring in the region of the trimethylsilyl and dinitrobenzenesulfonate substituents in **20** [C(6)–C(1)–C(2)–C(3) = 50.9(2)°] and a substantial opening of the Si–C–C angles. As a consequence, the Si–C(2)–C(1)–O(1) dihedral angle in **20** is reduced from 180° to –160.83(12)°. Inspections of the structural parameters in Tables 1 and 2 indicate the presence of similar structural distortions from the idealized chair geometry in the trimethylgermyl-substituted esters **18** and **19**.

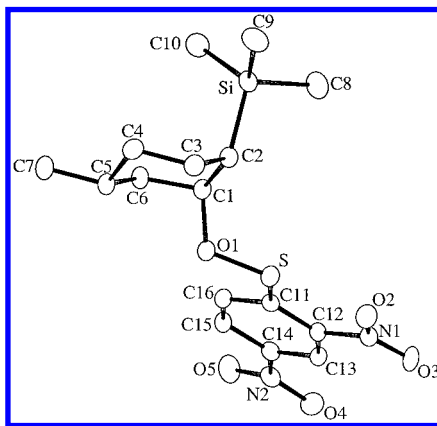
The geometry about the S–O bond in the three dinitrobenzenesulfonate esters as represented by the C(1)–O(1)–S–C(11) dihedral angle is 98.6° in **20**, 99.2° in **19**, and –99.5° in **21**. This conformation is presumably



**Figure 2.** Thermal ellipsoid plot for **18**. Ellipsoids are drawn at the 50% probability level.



**Figure 3.** Thermal ellipsoid plot for **19**. Ellipsoids are drawn at the 50% probability level.



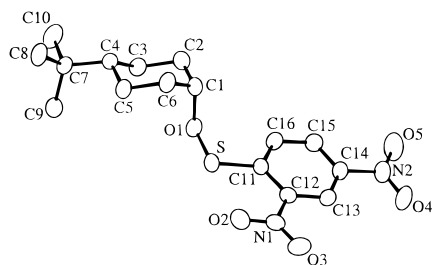
**Figure 4.** Thermal ellipsoid plot for **20**. Ellipsoids are drawn at the 50% probability level.

avored as it acts to minimize lone pair repulsion between the p-type lone pairs on the sulfur and the oxygen atoms of the sulfonate group.<sup>15</sup> The S–O bond is essentially coplanar with the aromatic ring in all three structures: the O(1)–S–C(11)–C(16) dihedral angle is 0.5(2)° for **19**, 0.1(2)° for **20**, and 2.75(12)° for **22**, allowing for maximum delocalization of the sulfur lone pair into the electron deficient benzene ring in all three structures. Both the 2- and 4-nitro groups are essentially coplanar with the aromatic ring in the sulfonates **19–21**; interestingly, this results in one of the 2-nitro oxygens, O(2), coming into very close contact with the adjacent sulfur atom.

(13) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratories: Oak Ridge, TN, 1965.

(14) We have previously estimated the contributions that induction and hyperconjugation make to the stabilization of positive charge by  $\beta$ -silicon, on the basis of structural geometries similar to these.<sup>6</sup> Thus, on the basis of the data of Lambert *et al.*<sup>4</sup> we estimate that with a Si–C–C–O dihedral angle of 180° vertical acceleration of unimolecular solvolyses of up to ca.  $6.2 \times 10^{12}$  (in addition to contributions from induction of ca. 75) might be observed.

(15) Wolfe, S. *Acc. Chem. Res.* **1972**, 5, 102.



**Figure 5.** Thermal ellipsoid plot for **21**. Ellipsoids are drawn at the 50% probability level.

**Table 1.** Selected Bond Lengths (Å), Bond Angles (Deg), and Dihedral Angles (Deg) for Compound **18**

Ge–C(2)	1.985(2)	Ge–CH <sub>3</sub> (av)	1.948
C(1)–O(1)	1.485(2)	C(1)–C(2)	1.513(2)
Ge–C(2)–C(1)	111.52(10)	Ge–C(2)–C(3)	115.10(10)
O(1)–C(1)–C(2)	107.11(11)	O(1)–C(1)–C(6)	107.55(12)
C(1)–C(2)–C(3)	111.67(12)	C(2)–C(3)–C(4)	113.21(12)
C(3)–C(4)–C(5)	111.68(13)	C(4)–C(5)–C(6)	108.46(12)
C(5)–C(6)–C(1)	113.18(12)	C(6)–C(1)–C(2)	113.71(12)
Ge–C(2)–C(1)–O(1)	–158.95(9)	Ge–C(2)–C(1)–C(6)	82.38(13)
Ge–C(2)–C(3)–C(4)	–78.97(14)	C(1)–C(2)–C(3)–C(4)	49.5(2)
C(2)–C(3)–C(4)–C(5)	–55.3(2)	C(3)–C(4)–C(5)–C(6)	56.8(2)
C(4)–C(5)–C(6)–C(1)	–55.9(2)	C(5)–C(6)–C(1)–C(2)	52.9(2)
C(6)–C(1)–C(2)–C(3)	–48.0(2)	O(1)–C(1)–C(2)–C(3)	70.7(2)
O(1)–C(1)–C(6)–C(5)	–65.5(2)		

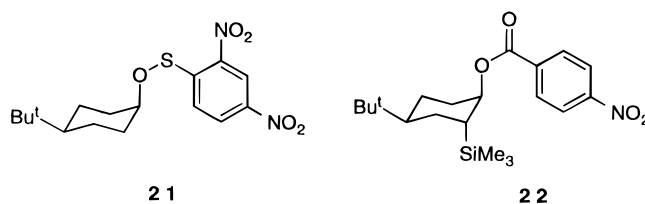
The O(2)⋯S nonbonded distances for **19–21** are remarkably short: 2.470, 2.473, and 2.480 Å, respectively. These are well within the sum of the van der Waals radii of S and O, which is 3.32 Å (1.52 Å for O and 1.8 Å for S),<sup>16</sup> suggesting a significant stabilizing interaction between the nitro oxygen O(2) and the sulfenyl sulfur as represented by Figure 6. Consistent with this is the observation that the O(2)–N(1) distance for **19–21** (average 1.236 Å) is significantly longer than the O(3)–N(1) distance (average 1.225 Å). Furthermore, the C(12)–N(1) distance for **19–21** (average 1.448 Å) is consistently shorter than the C(14)–N(2) distance (average 1.464 Å), implying a greater degree of delocalization of the sulfur lone pair onto the 2-NO<sub>2</sub> oxygens than onto the 4-NO<sub>2</sub> oxygens. The C–C bond lengths of the aromatic ring in **19–21** show a similar pattern of variation and are consistent with significant delocalization of the sulfur lone pair into the aromatic ring. The O(2)⋯S–O(1) angle in all three structures is close to 180°; this is a favorable geometry for interaction between the 2-nitro oxygen and sulfur d and p orbitals or, alternatively, interaction with the low-lying σ\* (S–O) orbital, which has been suggested.<sup>17</sup>

The C(alkyl)–O(ester) bond lengths for the β-(trimethylsilyl)-substituted sulfenylate **20** and the corresponding β-(trimethylgermyl) sulfenylate **19** are 1.490(3) and 1.492(2) Å, respectively; these do not differ significantly from each other but are significantly lengthened relative to the unsubstituted derivative **21**, which has a C–O bond length of 1.476(2) Å; more significant lengthening might well be expected if these systems had an ideal 180° geometry. The β-(trimethylgermyl)-substituted *p*-nitrobenzoate ester **18** has a C–O bond length of 1.485(2) Å; this is significantly lengthened relative to the unsubstituted derivative **5**,<sup>18</sup> which has a C–O bond length of

**Table 2.** Selected Bond Lengths (Å), Bond Angles (Deg), and Dihedral Angles (Deg) for the 2,4-Dinitrobenzenesulfenylate Esters **19**, **20**, and **21**

	<b>19</b> (M = Ge)	<b>20</b> (M = Si)	<b>21</b>
M–C(2)	1.992(2)	1.911(2)	
M–CH <sub>3</sub> (av)	1.945	1.865	
C(1)–O(1)	1.492(2)	1.490(3)	1.476(2)
C(11)–C(12)	1.411(3)	1.409(3)	1.405(2)
C(12)–C(13)	1.384(3)	1.383(3)	1.388(2)
C(13)–C(14)	1.371(3)	1.378(3)	1.369(2)
C(14)–C(15)	1.396(3)	1.394(3)	1.390(2)
C(15)–C(16)	1.380(3)	1.379(3)	1.377(2)
C(11)–C(16)	1.411(3)	1.413(3)	1.401(2)
C(12)–N(1)	1.449(2)	1.452(2)	1.442(2)
C(14)–N(2)	1.467(2)	1.461(2)	1.465(2)
N(1)–O(2)	1.235(2)	1.233(2)	1.240(2)
N(1)–O(3)	1.228(2)	1.229(2)	1.219(2)
N(2)–O(4)	1.227(2)	1.227(2)	1.220(2)
N(2)–O(5)	1.225(2)	1.225(2)	1.222(2)
C(11)–S	1.750(2)	1.749(2)	1.7533(14)
O(2)⋯S	2.470(2)	2.473(2)	2.480(2)
M–C(2)–C(1)	112.53(13)	113.6(2)	
M–C(2)–C(3)	114.77(13)	116.34(13)	
O(1)–C(1)–C(2)	110.0(2)	110.4(2)	105.15(12)
O(1)–C(1)–C(6)	104.7(2)	104.8(2)	110.80(12)
C(1)–C(2)–C(3)	111.1(2)	110.6(2)	112.56(12)
C(2)–C(3)–C(4)	111.4(2)	111.3(2)	111.86(13)
C(3)–C(4)–C(5)	111.1(2)	110.8(2)	108.69(11)
C(4)–C(5)–C(6)	109.4(2)	109.9(2)	112.24(12)
C(5)–C(6)–C(1)	113.6(2)	113.5(2)	111.90(12)
C(6)–C(1)–C(2)	113.7(2)	113.3(2)	111.33(12)
C(1)–O(1)–S	114.40(12)	114.60(11)	116.39(9)
O(1)–S–C(11)	100.07(9)	100.04(8)	100.09(6)
O(2)⋯S–O(1)	177.0(2)	177.0(2)	174.8(2)
M–C(2)–C(1)–O(1)	–162.16(12)	–160.83(12)	
M–C(2)–C(1)–C(6)	80.8(2)	82.1(2)	
M–C(2)–C(3)–C(4)	–75.2(2)	–76.1(2)	
C(1)–C(2)–C(3)–C(4)	54.0(2)	55.3(2)	55.2(2)
C(2)–C(3)–C(4)–C(5)	–58.6(2)	–59.3(2)	–55.8(2)
C(3)–C(4)–C(5)–C(6)	56.8(2)	56.8(2)	56.5(2)
C(4)–C(5)–C(6)–C(1)	–52.4(2)	–52.7(2)	–56.0(2)
C(5)–C(6)–C(1)–C(2)	49.8(2)	50.7(2)	52.7(2)
C(6)–C(1)–C(2)–C(3)	–49.5(2)	–50.9(2)	–52.7(2)
O(1)–C(1)–C(2)–C(3)	67.5(2)	66.3(2)	67.4(2)
O(1)–C(1)–C(6)–C(5)	–70.3(2)	–69.7(2)	–63.9(2)
C(11)–C(12)–N(1)–O(2)	–3.6(3)	–2.8(3)	0.2(2)
O(5)–N(2)–C(14)–C(15)	–4.2(3)	–4.3(3)	2.7(2)
O(1)–S–C(11)–C(16)	0.5(2)	0.1(2)	2.75(12)
C(1)–O(1)–S–C(11)	99.19(13)	98.60(13)	–95.88(10)

1.473(2) Å, but compares with the corresponding trimethylsilyl derivatives **4** (1.490(2) Å) and **22** (1.483(3) Å) (mean C–O 1.487 Å).



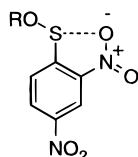
## Discussion

The C(alkyl)–O(ester) bond lengths of the two β-(trimethylgermyl) esters **18** and **19** are significantly lengthened relative to the corresponding unsubstituted esters **5**<sup>6</sup> and **21**; this indicates the presence of significant σ<sub>C–Ge</sub> – σ\*<sub>C–O</sub> hyperconjugative-like interactions between the high-lying C–Ge bonding orbital and the low-lying C–O

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(17) Kucsman, A.; Kapovits, I.; Parkanyi, L.; Argay, G. Y.; Kalman, A. *J. Mol. Struct.* **1984**, *125*, 331.

(18) White, J. M.; Robertson, G. B. *Acta Crystallogr., Sect. C* **1993**, *49*, 347.



**Figure 6.** Interaction between the 2-nitro oxygen and the sulfur in the 2,4-dinitrobenzenesulfenates **19**, **20**, and **21**.

antibonding orbital in these structures. The observed lengthening (and hence weakening) of the C–O bond lengths of **18** and **19** in the ground state is consistent with the enhanced reactivity of  $\beta$ -(trimethylgermyl) esters toward unimolecular solvolysis in solution.<sup>7</sup> The C–O bond lengths for **18** and **19** are, however, similar to the corresponding silicon-substituted esters **4**<sup>6</sup> and **20**, suggesting similar ground state effects of trimethylsilyl and trimethylgermyl substituents. The relative reactivities of  $\beta$ -(trimethylgermyl) esters,  $\beta$ -(trimethylsilyl) esters, and corresponding unsubstituted esters toward unimolecular solvolysis are ca.  $10^{14}$ : $10^{12}$ :1.<sup>2,4,7</sup> Given that a trimethylsilyl substituent lengthens C–O bonds at the  $\beta$  position by ca. 0.017 Å relative to the corresponding unsubstituted esters, any extra effects of a trimethylgermyl substituent are clearly too small to be detected by X-ray crystallography. However,  $\beta$ -(trimethylstannyl) esters have relative rates of unimolecular solvolysis of  $\gg 10^{14}$  relative to unsubstituted esters and are expected to show very significant ground state effects; unfortunately, however, these compounds are too reactive to allow the preparation of crystals suitable for X-ray structural analysis.

### Conclusion

The presence of a  $\beta$ -(trimethylgermyl) substituent causes significant lengthening of ester C–O bond lengths in the antiperiplanar geometry, relative to the corresponding unsubstituted esters. This is consistent with the observed enhanced reactivity of  $\beta$ -(trimethylgermyl) esters toward unimolecular solvolysis. The effects of  $\beta$ -germanium are similar to the effects of  $\beta$ -silicon.

### Experimental Section

**(a) Crystallography.** Diffraction data were recorded on an Enraf-Nonius CAD4f diffractometer operating in the  $\theta/2\theta$  scan mode at low temperature (130 K) for **18**–**20**. The unsubstituted sulfonate **21** underwent a destructive phase change below 150 K; thus, data were collected at 200 K. Data were corrected for Lorentz and polarization effects and for absorption (SHELX 76).<sup>19</sup> Structures were solved by direct methods (SHELXS-86)<sup>20</sup> and were refined on  $F^2$  (SHELXL-93).<sup>21</sup> Crystal data and refinement details for **18**–**21** are listed in Table 3.

**(b) Synthesis.** General experimental details are as reported in a previous paper.<sup>22</sup>

(19) SHELX76: Sheldrick, G. M. *Program for Crystal Structure Determination*; Cambridge, England, 1976.

(20) SHELXS-86: Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189.

(21) SHELXL-93: Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1993.

(22) Green, A. J.; Kuan, Y. L.; White, J. M. *J. Org. Chem.* **1995**, *60*, 2734.

(23) The author has deposited atomic coordinates for **18**–**21** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

**trans-4-Methylcyclohexene oxide (15).** A solution of 4-methylcyclohexene (95.64 g, 0.996 mol), acetonitrile (182 mL, 3.49 mol), hydrogen peroxide (155 mL, 30%), potassium bicarbonate (25 g), and methanol (1.5 L) was stirred at room temperature for 70 h. The mixture was diluted with an equal volume of water and then extracted with chloroform ( $4 \times 150$  mL). The combined organic extracts were washed with water ( $3 \times 100$  mL), dried ( $\text{MgSO}_4$ ), and evaporated down to yield a ca. 1:1 mixture of *cis*- and *trans*-epoxides as a clear oil (78.4 g, 70%): <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  53.03, 52.18, 51.77, 51.37, 33.54, 32.45, 28.94, 27.57, 26.38, 25.17, 24.22, 23.37, 21.95, 21.57; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  0.84 (d, 3H,  $\text{CH}_3$ ), 1.2–1.9 (m, 7H), 3.2 (m, 2H).

The *cis/trans* mixture of epoxides (72.94 g, 0.651 mol) and *p*-nitrobenzoyl chloride (186.2 g, 1.00 mol) were dissolved in chloroform (1.5 L). With constant stirring, a steady stream of anhydrous hydrogen chloride gas was passed through the solution over a period of 6 h. The resulting solution was then washed with water ( $3 \times 200$  mL) to remove the excess acid and was then dried ( $\text{MgSO}_4$ ). The residue was taken up in pyridine (80 mL) and was stirred for 30 min. Water (60 mL) was then added to the solution, which was then allowed to stir for a further 1.5 h to decompose the excess acid chloride. The mixture was then taken up in ether (100 mL) and washed with hydrochloric acid (1 M,  $3 \times 200$  mL), 10% sodium bicarbonate ( $3 \times 200$  mL), and water (200 mL). After drying ( $\text{MgSO}_4$ ), evaporation of the ether under reduced pressure gave an ca. 1:1 mixture of the chloroesters **16** and **17** (162 g, 84%). Fractional recrystallization of the crude product from methanol gave pure crystals of the desired chloroester **16** (18.58 g, 10%): mp (MeOH) 100.5–101.5 °C; IR  $\nu_{\text{max}}$  1525, 1334 ( $\text{NO}_2$ ), 1720 (C=O), 1273 (CO)  $\text{cm}^{-1}$ ; <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  163.4, 150.58, 135.45, 130.67, 123.51, 74.02, 56.78, 33.44, 29.30, 28.19, 26.78, 21.13; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  0.9 (d, 3H,  $\text{CH}_3$ ), 1.45–2.05 (m, 7H), 4.2 (m 1H), 5.3 (m, 1H), 8.2 (d, 2H), 8.3 (d, 2H). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}_4\text{Cl}$ : C, 56.50; H, 5.41; N, 4.70; Cl, 11.9. Found: C, 56.50; H, 5.38; N, 4.65; Cl, 11.87.

The chloro ester **16** (18.0 g, 0.061 mol) and potassium carbonate (22 g in 24 mL of water) were refluxed in methanol (200 mL) for 2 h with rapid stirring. The solution was then taken up in an equal volume of water and extracted with pentane ( $3 \times 50$  mL). The combined pentane extracts were washed with water ( $3 \times 50$  mL), dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure to give the pure *trans*-epoxide **15** as a clear oil (5.3 g, 78%): IR  $\nu_{\text{max}}$  1255  $\text{cm}^{-1}$ ; <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  53.07, 51.43, 33.65, 29.03, 24.29, 23.47, 21.66; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  0.84 (d, 3H,  $\text{CH}_3$ ), 1.21–1.99 (m, 7H), 3.12 (m, 2H).

**r-5-tert-Butyl-c-2-(trimethylgermyl)cyclohexan-t-ol (9).** A suspension of lithium metal (0.35 g, 0.05 mol, 15 equiv) in HMPA (14 mL) under nitrogen gas was sonicated until it went dark blue in color. To this solution was added bromotrimethylgermane (1.0 mL, 0.007 mol, 2.3 equiv), whereupon the solution developed a golden yellow color. THF (200 mL) was then added, and the solution was left to stir for 5 h. The mixture was cooled to 0 °C, and *trans*-4-tert-butylcyclohexene oxide (**14**) (0.5 g, 0.032 mol) was added and then stirred overnight. Water (100 mL) was added, then the resulting mixture was extracted with ether ( $3 \times 100$  mL). The combined organic extracts were washed with water ( $3 \times 100$  mL), dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure to leave **9** as a white solid that was pure by NMR (0.84 g, 95%): mp 47–48 °C; IR  $\nu_{\text{max}}$  3323 (OH), 823.0 s, 1233 s, ( $\text{GeC}$ )  $\text{cm}^{-1}$ ; <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  69.39, 40.69, 33.94, 32.21, 32.09, 27.32, 24.84, 22.54, –1.59; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  0.15 (s, 9H), 0.82 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 0.85–2.01 (m, 8H), 4.19 (m, 1H, HCO).

**r-5-Methyl-c-2-(trimethylstannyl)cyclohexan-t-ol (12).** To a suspension of lithium metal (1.250 g, 0.18 mol, 17 equiv) in THF (40 mL) was added trimethyltin chloride (26 mL, 1 M in THF, 0.026 mol). The resulting solution was sonicated under nitrogen gas for 3.5 h. The solution was filtered, cooled to 0 °C, and then treated with *trans*-4-methylcyclohexene oxide (**15**) (1.2 g, 0.011 mol). After being stirred for 15 h, the reaction was quenched with water (100 mL) and extracted with ether ( $3 \times 100$  mL). The combined ether extracts were dried ( $\text{MgSO}_4$ ) and evaporated under reduced pressure to give the

Table 3. Crystal Data and Structure Refinement Details for Compounds 18–21

	18	19	20	21
emp formula	C <sub>20</sub> H <sub>31</sub> NO <sub>4</sub> Ge	C <sub>16</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> SGe	C <sub>16</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> SSi	C <sub>16</sub> H <sub>22</sub> N <sub>2</sub> O <sub>5</sub> S
formula wt	422.07	429.05	384.53	354.43
temp (K)	130(1)	130(1)	130(1)	200(1)
radiatn	Cu K $\alpha$	Mo K $\alpha$	Cu K $\alpha$	Cu K $\alpha$
wavelength (Å)	1.541 80	0.709 30	1.541 80	1.5418
crystal syst	monoclinic	monoclinic	monoclinic	triclinic
space grp	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1
unit cell dims				
a (Å)	6.2268(8)	14.016(2)	13.941(4)	8.164(12)
b (Å)	18.434(3)	12.772(4)	12.747(3)	10.968(4)
c (Å)	18.681(2)	11.429(4)	11.414(4)	11.590(2)
$\alpha$ (deg)				111.59(2)
$\beta$ (deg)	98.568(9)	113.96(2)	113.61(3)	99.64(2)
$\gamma$ (deg)				110.13(2)
vol (Å <sup>3</sup> )	2120.3(4)	1869.7(9)	1858.5(9)	853.1(3)
<i>Z</i>	4	4	4	2
<i>D</i> <sub>c</sub> (Mg/m <sup>3</sup> )	1.32	1.524	1.374	1.380
$\mu$ (mm <sup>-1</sup> )	2.15	1.778	2.423	1.943
<i>F</i> (000)	888	888	816	376
cryst size (mm)	0.48 × 0.36 × 0.45	0.41 × 0.41 × 0.64	0.29 × 0.26 × 0.23	0.46 × 0.27 × 0.12
$\theta$ range for data collectn	3.39–74.97	2.25–29.90	3.46–75.00	4.36–74.84
index ranges	–7 ≤ <i>h</i> ≤ 7 –23 ≤ <i>k</i> ≤ 23 0 ≤ <i>l</i> ≤ 23	0 ≤ <i>h</i> ≤ 19 –17 ≤ <i>k</i> ≤ 0 –16 ≤ <i>l</i> ≤ 14	–17 ≤ <i>h</i> ≤ 17 –15 ≤ <i>k</i> ≤ 15 –14 ≤ <i>l</i> ≤ 14	0 ≤ <i>h</i> ≤ 10 –13 ≤ <i>k</i> ≤ 12 –14 ≤ <i>l</i> ≤ 14
no. intens controls	3	3	3	3
interval (min)	160	160	160	160
dec	insignificant	insignificant	insignificant	insignificant
absorptn method	SHELX76	SHELX76	SHELX76	SHELX76
max, min transmission	0.503, 0.329	0.88, 0.48	0.65, 0.52	0.81, 0.47
reflns collected	8926	5617	8986	3765
independent reflns	4361	5417	3832	3507
	[ <i>R</i> (int) = 0.0167]	[ <i>R</i> (int) = 0.0284]	[ <i>R</i> (int) = 0.0576]	[ <i>R</i> (int) = 0.0116]
no. of obsd reflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	4262	4242	3803	3389
refinement method	full-matrix on <i>F</i> <sup>2</sup>	full-matrix on <i>F</i> <sup>2</sup>	full-matrix on <i>F</i> <sup>2</sup>	full-matrix on <i>F</i> <sup>2</sup>
data/restraints/params	4361/0/360	5417/0/323	3832/0/323	3506/0/306
GOF on <i>F</i> <sup>2</sup>	0.957	1.044	1.118	1.035
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0261 <i>wR</i> <sub>2</sub> = 0.0690	<i>R</i> <sub>1</sub> = 0.0341 <i>wR</i> <sub>2</sub> = 0.0684	<i>R</i> <sub>1</sub> = 0.0539 <i>wR</i> <sub>2</sub> = 0.1357	<i>R</i> <sub>1</sub> = 0.0344 <i>wR</i> <sub>2</sub> = 0.1278
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0280 <i>wR</i> <sub>2</sub> = 0.0702	<i>R</i> <sub>1</sub> = 0.0546 <i>wR</i> <sub>2</sub> = 0.0760	<i>R</i> <sub>1</sub> = 0.0541 <i>wR</i> <sub>2</sub> = 0.1359	<i>R</i> <sub>1</sub> = 0.0354 <i>wR</i> <sub>2</sub> = 0.1332
weighting scheme				
$w = 1/[\sigma^2(F_o^2) + (A^*P)^2 + B^*P]$	<i>A</i> = 0.0398	<i>A</i> = 0.0322	<i>A</i> = 0.0705	<i>A</i> = 0.102
where $P = (F_o^2 + 2F_c^2)/3$	<i>B</i> = 1.321	<i>B</i> = 0.9241	<i>B</i> = 1.1806	<i>B</i> = 0.1237
extinction method	SHELXL	SHELXL	SHELXL	SHELXL
extinction coefficient	0.0037(2)	0.000	0.0023(4)	0.013(2)
maximum shift/esd	0.365	0.064	0.035	–0.005
largest diff peak and hole (e Å <sup>-3</sup> )	0.278 and –0.336	0.540 and –0.416	0.866 and –0.661	0.287 and –0.345

crude alcohol (4.77 g) as a light yellow oil. Purification by Kugel distillation (2 mmHg, 100 °C) yielded the pure alcohol **12** (2.97 g, 100%) as a colorless oil: IR  $\nu_{\max}$  3334 (OH), 763.0, 1260 (SnC) cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  70.28, 41.57, 33.86, 33.63, 27.10, 23.64, 21.22, –9.93; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.0 (s, 9H), 0.90 (d, 3H), 1.4–2.1 (m, 8H), 4.02 (m, 1H). Anal. Calcd for C<sub>10</sub>H<sub>22</sub>OSn: C, 43.36; H, 8.01. Found: C, 42.87; H, 8.26.

**r-5-tert-Butyl-c-2-(trimethylstannyl)cyclohexan-tol (11).** To a suspension of lithium metal (0.625 g, 0.009 mol, 10 equiv) in THF (40 mL) was added trimethyltin chloride (13 mL, 1 M in THF, 0.013 mol), and the mixture was sonicated under nitrogen gas for 2 h and then left to stir overnight. The resulting blue solution was filtered under nitrogen and cooled to 0 °C, and then *trans*-4-*tert*-butylcyclohexene oxide (**14**) (1.00 g, 0.009 mol) was added. After being stirred for 24 h, the reaction was quenched with water (100 mL) and extracted with ether (3 × 100 mL). The ether extracts were dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the crude alcohol (2.40 g) as a light yellow oil. Purification by distillation under reduced pressure gave the pure alcohol **11** as a waxy solid: IR  $\nu_{\max}$  3330 (OH), 763.0, 1235 (SnC) cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  70.77 (CO), 40.97, 33.11, 32.62, 32.21, 27.36 (CH<sub>3</sub>)<sub>3</sub>, 26.27, 23.94, –9.57 (Sn(CH<sub>3</sub>)<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.10 (s, 9H, Sn(CH<sub>3</sub>)<sub>3</sub>), 0.85 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.2–2.2 (m, 8H, 4.27 (1H, m).

**r-5-tert-Butyl-c-2-(trimethylgermyl)cyclohex-t-yl p-Nitrobenzoate (18).** A solution of the 5-*tert*-butyl-2-(trimethylgermyl) alcohol **9** (200 mg, 0.73 mmol) in pyridine (1

mL) stirred at 0 °C was treated with *p*-nitrobenzoyl chloride (184 mg, 1.2 equiv). The resulting slurry was stirred at room temperature for 5 h and then treated with water (0.5 mL) and stirred for a further 20 min. The slurry was diluted with water (20 mL) and extracted with ether (3 × 20 mL). The combined organic extracts were washed with HCl (1 M, 1 × 20 mL), saturated aqueous sodium bicarbonate (1 × 20 mL), and water (1 × 20 mL), dried (MgSO<sub>4</sub>), and evaporated to an oil that solidified. Recrystallization from ether/pentane gave **18** as white blocks (254 mg, 82%): mp 91–92 °C; IR  $\nu_{\max}$  1704 (C=O), 1526.0, 1342.0 (NO<sub>2</sub>), 822.0, 1180 (GeC) cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  164.01, 150.29, 136.73, 130.48, 123.46, 76.04, 42.08, 32.24, 30.90, 29.70, 27.28, 24.52, 23.51, –1.53 (Ge(CH<sub>3</sub>)<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.19 (s, 9H), 0.97 (s, 9H, CH<sub>3</sub>), 0.8–2.4 (m, 8H), 5.4 (m, 1H), 8.24 (d, 2H), 8.37 (d, 2H).

**r-5-Methyl-c-2-(trimethylgermyl)cyclohex-t-yl 2,4-Dinitrobenzenesulfenate (19).** To a stirred solution of the trimethylgermyl alcohol **10** (200 mg, 0.93 mmol) in dichloromethane (10 mL) in the presence of pyridine (0.5 mL) was added 2,4-dinitrobenzenesulfonyl chloride (261 mg, 1.1 mmol), and the mixture was then stirred for 18 h. The resulting mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 20 mL), and the combined organic extracts were washed with HCl (1 M, 1 × 20 mL) and saturated aqueous sodium bicarbonate (1 × 20 mL), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure to yield a bright yellow solid that was recrystallized from pentane, giving

**19** as bright yellow blocks (320 mg, 80%): mp 105–107 °C; IR  $\nu_{\text{max}}$  1511.0, 1339.0 (NO<sub>2</sub>), 815.0, 1233 (GeC) cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  155.54, 144.5, 139.6, 127.44, 123.86, 121.24, 86.58, 37.76, 32.24, 32.64, 26.68, 22.43, 21.97, -1.61; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.09 (9H, s), 0.9 (3H, d,  $J$  = 7.5 Hz), 0.8–2.1 (8H, m), 3.95 (1H, m), 7.9 (1H, d,  $J$  = 11 Hz), 8.4 (1H, br d,  $J$  = 11 Hz), 9.08 (1H, br s).

The same general procedure used for the preparation of **19** was employed for the preparation of the 2,4-dinitrobenzene-sulfenates **20** and **21**.

***r*-5-Methyl-*c*-2-(trimethylsilyl)cyclohex-*t*-yl 2,4-Dinitrobenzenesulfenate (20).** Prepared from the trimethylsilyl alcohol **13** and obtained as yellow blocks from pentane (80%): mp 64–67 °C dec; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  9.11 (1H, d,  $J$  = 2.5 Hz), 8.45 (1H, dd,  $J$  = 10, 2.5 Hz), 7.95 (1H, d,  $J$  = 10 Hz), 4.0 (1H, m), 2.2–1.0 (8H, m), 0.92 (3H, d,  $J$  = 7 Hz), 0.05 (9H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  155.4, 144.2, 139.3, 128.9, 123.9, 121.2, 85.97, 37.89, 32.26, 30.61, 26.64, 21.90, 21.54, -1.07.

***trans*-4-*tert*-Butylcyclohexyl 2,4-Dinitrobenzenesulfenate (21).** Prepared from *cis*-4-*tert*-butylcyclohexanol

and obtained as yellow blocks from methanol (85%): mp 161–163 °C dec; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  9.09 (1H, br s), 8.46 (1H, br d,  $J$  = 11 Hz), 7.95 (1H, d,  $J$  = 11 Hz), 3.92 (1H, m), 2.3–2.2 (2H, m), 1.7–1.3 (6H, m), 1.1–1.0 (1H, m), 0.88 (9H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  155.16, 144.29, 139.36, 127.59, 123.69, 121.18, 82.02, 47.49, 32.55, 31.29, 27.40, 21.19.

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**Supporting Information Available:** <sup>13</sup>C NMR spectra of **9–12**, **16**, and **18–21** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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