J. Org. Chem. **1998,** *63,* 3943−3951

Interaction of Trimethylsilyl and Trimethylstannyl Substituents with C−O Bonds at the γ Position. Results from X-ray Structural Studies and Solvolysis Studies

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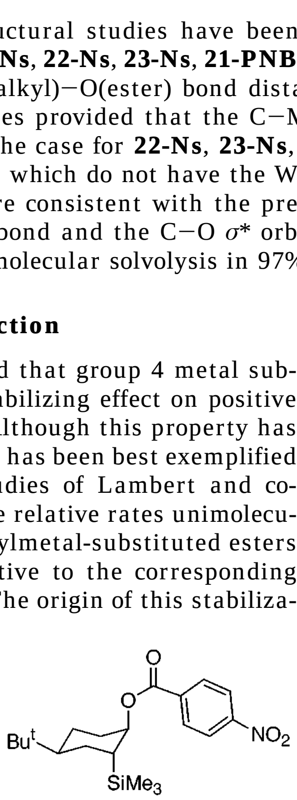
Received December 30, 1997

Accurate X-ray structural studies have been carried on the γ-Me$_3$M (M = Si, Sn)-substituted cyclohexyl esters **21-Ns**, **22-Ns**, **23-Ns**, **21-PNB**, and **24-PNB**. Analysis of the structural parameters reveals that the C(alkyl)−O(ester) bond distance is lengthened slightly compared to nonmetal-substituted analogues provided that the C−M, C−O, and intervening C−C bonds are in the W arrangement as is the case for **22-Ns**, **23-Ns**, and **24-Ns**. However, the C−O bond distances for **22-PNB** and **22-Ns**, which do not have the W geometry, are not significantly lengthened. These structural effects are consistent with the presence of a percaudel interaction between the back lobe of the C−M σ bond and the C−O σ* orbital. The γ-Me$_3$Sn cyclohexyl nosylates **21-Ns** and **23-Ns** undergo unimolecular solvolysis in 97% TFE/H$_2$O with relative rates ca. 1:>10 000.

Introduction

It has been well-established that group 4 metal substituents have a dramatic stabilizing effect on positive charge at the β position.[1−4] Although this property has been known for many years, it has been best exemplified by the elegant solvolysis studies of Lambert and coworkers.[3,5−9] For example, the relative rates unimolecular solvolysis of the β-trimethylmetal-substituted esters **1−3** are $\gg 10^{14}:10^{13}:10^{12}$ relative to the corresponding unsubstituted analogues.[5,6] The origin of this stabilization is believed to be due to hyperconjugation between the high-lying C−M σ bond and the carbenium ion p orbital. These huge rate enhancements observed by Lambert have their genesis in the ground state as has been demonstrated by low-temperature X-ray studies. The C(alkyl)−O(ester) bond is significantly lengthened, and hence weakened, by the presence of the β group 4 substituent.[2,10−12] For example, the C(alkyl)−O(ester) bond distances in the β-(trimethylsilyl) and β-(trimethylgermyl) *p*-nitrobenzoates **4** and **5** are 1.483(3) and 1.485(2) Å, respectively,[10] which are both significantly lengthened compared with the unsubstituted analogue **6** for which the corresponding distance is 1.473(2) Å.[13] The origin of the bond lengthening in **4** and **5** is believed to be due to $\sigma-\sigma$* interactions between the high-lying C−M (M = Si, Ge) σ orbital and the vacant low-lying C−O σ* orbital. Consistent with this interpretation is the absence of any significant effects on the C−O bond distance in the gauche β-silyl *p*-nitrobenzoate ester **7**, for which $\sigma_{C-Si} - \sigma^*_{C-O}$ overlap is negligible.[10] The interaction of group 4 metal substituents with positive charge at the γ position, although less dramatic than the β-effect, is also well established. Since Sommer and Whitmore[14] first revealed the ability of silicon to interact with positive charge at the γ position in 1946, group 4 substituents have been shown to have varying accelerative effects on

1; R = Bu^t, M = Si, R' = CF$_3$
2; R = H, M = Ge R' = CF$_3$
3; R = Bu^t, M = Sn, R' = CH$_3$



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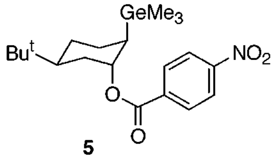

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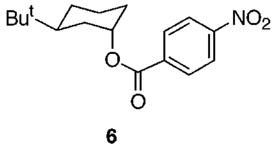

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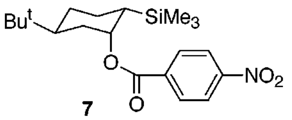

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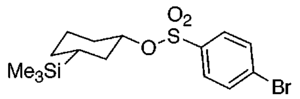

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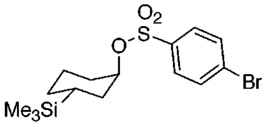

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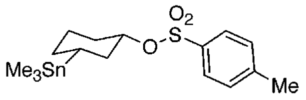

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* To whom correspondence should be addressed.

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

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

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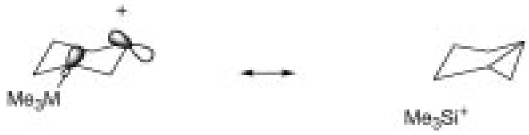


Figure 1. Stabilization of positive charge at the γ position by Homohyperconjugation.

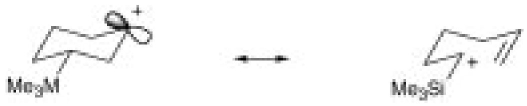
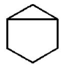


Figure 2. Stabilization by inductively enhanced C−C hyperconjugation.

the solvolysis rates of γ-disposed leaving groups, depending on the shape of the carbon framework in the system under investigation.[15−20] The stereochemical requirement of the group IV γ effect was first established by Shiner et al. using a series of γ-silicon substituted cyclohexyl *p*-bromobenzenesulfonates.[15,16] The presence of silicon in the γ position increases the rate of solvolysis of the *cis*-cyclohexyl brosylate **8** by a factor of 452 when both the brosylate and silicon substituents are equatorially disposed, so that the two substituents, with the two intervening C−C bonds, have a "W" relationship. Acceleration is not seen, however, when the C−O bond is axial as in the trans isomer **9**. It was later shown that this acceleration is raised to 2010-fold when the γ substituent is the trimethylstannyl group and the nucleofuge is *p*-toluenesulfonate as in **10**.[20] It has been suggested that during the solvolysis of **8** and **10** the γ-metal substituent stabilizes the developing carbocation by a through-space interaction between the back lobe of the C−M bond and the developing carbocation p orbital.[15−20] This type of participation is often referred to as percaudal (through the tail) homohyperconjugation, and the carbenium ion can be represented by the valence bond forms in Figure 1; this mode of participation is supported by the isolation of large quantities of bicyclo[3.1.0]hexane **11** among the solvolysis products of **8** and **10**.[15,16,20] An alternative suggestion is that the developing carbenium ion in these systems is stabilized by inductively enhanced C−C hyperconjugation (Figure 2). The electropositive metal substituent is proposed to raise the energy of the C_β−C_γ bond, resulting in a better energy match with the developing carbenium ion. However, a theoretical study on the 3-silaprop-1-yl cation **12** suggested partial bridging with a distance of 1.82 Å between the γ-carbon and the carbenium ion together with a high degree of positive charge on the silicon, consistent with the percaudel interaction.[19] The carbenium ion **12** was calculated to be 10 kcal/mol more stable than the 1-propylcarbenium ion **13**, and the C2−C3 bond distance was no longer than the corresponding distance for the 1-propylcarbenium ion **13**, indicating that the stabilizing effect of the silicon in **12** is not due to increased C−C hyperconjugation. The γ effect of silicon in the adamantyl framework **14** was studied by Grob et al.[21] and was found to be modest by comparison with the cyclohexyl framework; thus, the relative rates of solvolysis of **14** and the unsubstituted derivative **15** was only 8.6:1. It has been pointed out[22] that the smaller increase in solvolytic rates in the adamantyl system may be due to the fact that in both the silylated and unsilylated systems the carbocation would have three β antiperiplanar C−C bonds that could stabilize the positive charge by normal hyperconjugation, thereby reducing the demand on homohyperconjugative stabilization from the C−Si bond. However, a more frequently used explanation is that the rigid carbon framework constrains the C_α−C_γ distance to be ca. 2.4 Å, which would hinder overlap between the rear lobe of the C−Si bonding orbital and the developing carbocation p orbital. This idea is clearly supported in the studies of Adcock[22] and co-workers on the norbornyl triflates **16** and **17** where the C_α−C_γ distance is decreased. The presence of a trimethylsilyl group at the second bridgehead carbon of 1-norbornyl triflate increases the rate of solvolysis by 1319, and this factor is increased to 20 486 for a trimethylstannyl group. Ab initio theoretical calculations that accompany the kinetics data predict that the Cα−Cγ distance is about 2.3 Å in the parent compounds but that this distance is reduced to 1.9 Å in the silyl-substituted cation and to 1.8 Å in the stannyl-substituted case.



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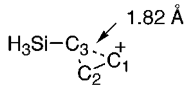

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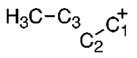

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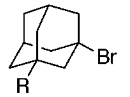
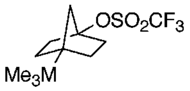


14 R = SiMe$_3$
15 R = H



16; M = Si
17; M = Sn

Given the effect that γ-group 4 metal substituents have on the reactivity of ester leaving groups toward unimolecular solvolysis, we were interested in determining whether there would be any observable ground-state effects associated with these substituents. In particular, we were interested to see whether the γ-metal substituent would cause any significant lengthening of the C(alkyl)−O(ester) bond distance and to determine the dependence of these effects (if present) upon geomety. We chose to study a selected range of γ-trimethyl metal cyclohexyl esters in which the metal and ester substituents are constrained to have the W relationship as in **18** and also a range of γ-trimethyl metal cyclohexyl esters in which the trimethyl metal substituent is constrained to take the axial orientation while the ester substituent is equatorial as typified by **19**. The two basic structures

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(15) Shiner, V. J., Jr.; Ensinger, M. W.; Kris, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842.

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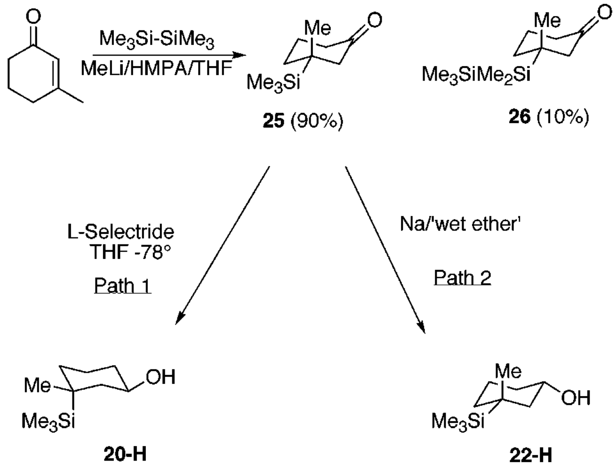
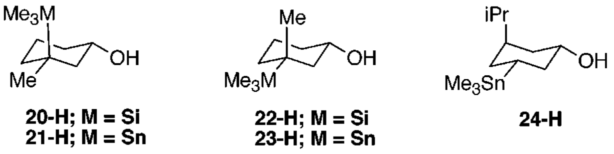
Figure 3. Interaction of C−O σ^* antibonding orbital with the backlobe of the C−M bond **18** or with the C_γ-C_β bond **19**.

Scheme 1



18 and **19** would allow the separation of the effects (if any) from a percaudel-like interaction between the C−M σ orbital and the C−O σ^* orbital and inductively enhanced C−C hyperconjugation between the C_γ−C_β σ bond and the C−O σ^* orbital (Figure 3).

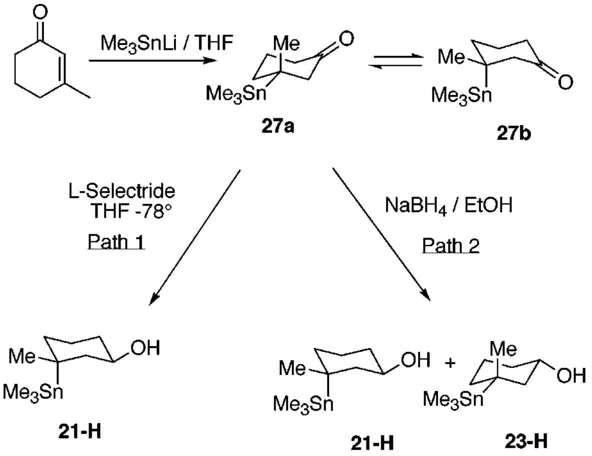
To this end, we set out to prepare the model γ-silyl- and the γ-stannylcyclohexanols **20-H**−**24-H** with a view to determining the structures of their ester derivatives.



Synthesis

The axial and equatorial γ-silyl alcohols **20-H** and **22-H** were synthesized according to Scheme 1. (Trimethylsilyl)lithium was generated from hexamethyldisilane and methyllithium[23] in HMPA/THF and then treated with commercially available 3-methyl-2-cyclohexenone, giving the β-silyl ketone **25** along with a small quantity of the pentamethyldisilanyl ketone **26**. The two ketones were readily separated by vacuum distillation. The ^{13}C δ value for the Me_3Si methyls in **25** appeared at −4.99 ppm; this high-field shift is consistent with an equatorially disposed trimethylsilyl substituent, suggesting that the ketone **25** exists substantially in the chair conformation having the silyl substituent equatorial.[24] Consistent with the trimethylsilyl group being equatorial was the observation that reduction of **25** with L-Selectride in THF at −78 °C (Scheme 1, path 1) gave entirely the axial γ-silyl alcohol **20-H** by approach of the bulky hydride reagent from the face opposite the axial methyl substituent. Reduction of the β-silyl ketone **25** with sodium in wet ether (Scheme 1, path 2) gave the equatorial γ-silyl alcohol **22-H** as the major product in >90% yield.

Scheme 2



The axial and equatorial γ-stannyl alcohols **21-H** and **23-H** were prepared according to Scheme 2. Conjugate addition of (trimethylstannyl)lithium to 3-methyl-2-cyclohexenone gave the β-stannylcyclohexanone **27** in 90% yield. The ^{13}C δ value for the Me_3Sn methyls in **27** appeared at −11.03 ppm. Given that axially disposed cyclohexyl trimethystannyl substituents generally absorb in the range −9 to −10 ppm and equatorial trimethylstannyl substituents absorb in the range −11 to −12 ppm, the value of −11.03 ppm suggests that **27** exists with a significant population of the conformation **27a**. The conformational *A* values for a trimethylstannyl substituent and a methyl substituent are 0.95 and 1.74 kcal/mol, respectively,[24] which leads to the prediction that the axial conformation **27b** should be substantially more stable because it is less strained sterically than the equatorial conformation **27a**. It is possible that the equatorial conformation **27a** is stabilized by a percaudel interaction between the C−Sn σ bonding orbital and the carbonyl π^* orbital. Reduction of the β-stannylcyclohexanone **27** with L-Selectride at −78 °C (Scheme 2, path 1) gave the axial stannylcyclohexanol derivative **21-H** as the only product detectable by NMR, suggesting that all reaction with the bulky hydride-reducing agent occurred from the equatorial conformation. Attempts were made to prepare the equatorial stannylcyclohexanol **23-H** by reduction of the β-stannyl ketone **27** with sodium in wet ether as in the preparation of the equatorial silyl alcohol. However, this failed to give the equatorial γ-stannyl alcohol **23-H** and instead gave rise to a complex mixture possibly resulting from reductive cleavage of the C−Sn bond. The equatorial γ-stannyl alcohol **23-H** was, however, successfully prepared as a ca. 1:1 mixture with the axial γ-stannylcyclohexanol **21-H** by reduction of **27** with sodium borohydride (Scheme 2, path 2), separation of **21-H** and **23-H** was readily achieved by chromatography.

The alcohol **24-H** was prepared according to Scheme 3. Conjugate addition of (trimethylstannyl)lithium to 5-isopropyl-2-cyclohexenone gave a ca. 4:1 mixture of *trans*-5-isopropyl-3-(trimethylstannyl)cyclohexanone (**28**) and the cis isomer **29**. This mixture was not separated but was reduced using sodium borohydride in ethanol to afford a mixture of the alcohols **24-H** and **30-H** in a ratio of ca. 1.2:1 (from reduction of ketone **28**) and a smaller amount of **31-H** (from ketone **29**). These structures were tentatively assigned by comparison of their ^{13}C NMR data

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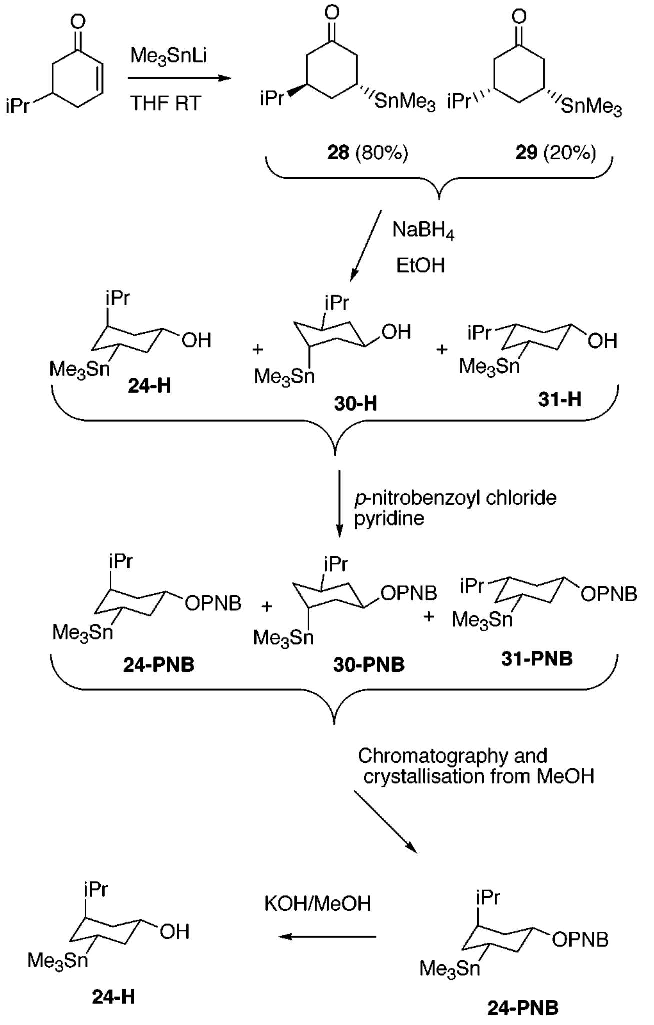
[23] Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69.

[24] Wickham, G.; Olszowy, H. A.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 3788.

Scheme 3



with those of the corresponding 5-methyl-3-(trimethylstannyl)cyclohexanols.[24] This mixture of alcohols unfortunately was inseparable and was converted to the corresponding mixture of *p*-nitrobenzoate ester derivatives **24-PNB**, **30-PNB**, and **31-PNB**. Partial separation of these esters by chromatography followed by repeated recrystallization gave pure crystals of the *p*-nitrobenzoate ester derivative **24-PNB** of the alcohol **24-H**, which were used for X-ray structural analysis (below). Hydrolysis of **24-PNB** gave pure **24-H**.

The alcohols **20-H**–**24-H** were converted to the corresponding *p*-nitrobenzenesulfonate derivatives **20-Ns**–**24-Ns** by reaction with *p*-nitrobenzenesulfonyl chloride in pyridine; the nosylates **21-Ns**–**23-Ns** gave crystals suitable for X-ray analysis; however, the axial silicon nosylate **20-Ns** consistently gave powders upon recrystallization, while the equatorial stannyl nosylate **24-Ns** decomposed during crystallization. The axial stannyl *p*-nitrobenzoate **21-PNB** was prepared under standard conditions and gave crystals that were used suitable for crystallographic analysis.

Molecular Structures

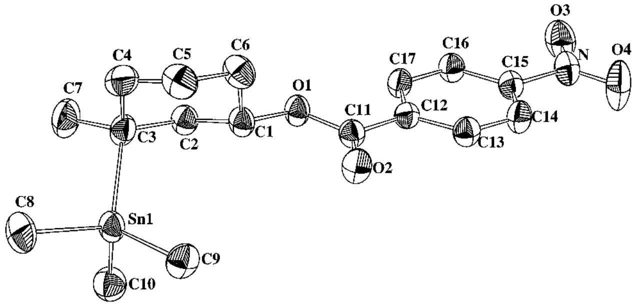
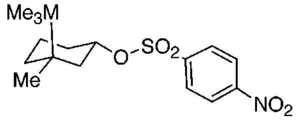
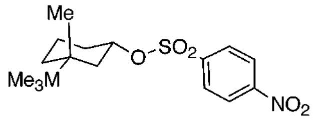


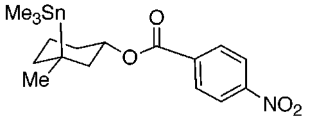
Figure 4. Thermal ellipsoid plot for compound **21-PNB**.



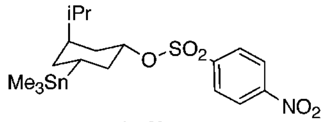
20-Ns; M = Si
21-Ns; M = Sn



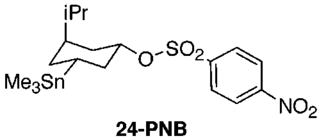
22-Ns; M = Si
23-Ns; M = Sn



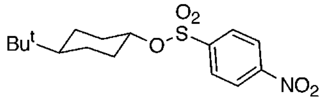
21-PNB



24-Ns



24-PNB



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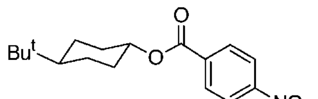
The structures of **21-Ns**, **22-Ns**, **23-Ns**, and **24-PNB** were determined at 130.0 K to remove unwanted thermal effects. The *p*-nitrobenzoate ester **21-PNB** underwent a destructive phase change upon cooling; therefore, the structure of **21-PNB** was determined at room temperature. The structures **21-PNB**, **21-Ns**, **22-Ns**, **23-Ns**, and **24-PNB** are presented in Figures 4–8, respectively, which depict 30% ellipsoids drawn using the program ZORTEP.[25] Hydrogen atoms (which were refined isotropically) are omitted for clarity. Selected bond lengths for **21-PNB**, **21-Ns**, **22-Ns**, **23-Ns**, and **24-PNB** are presented in Table 1. The data for the corresponding nonmetalated nosylate derivatives **32**[26] and *p*-nitrobenzoate derivative **33**,[13] which have been reported elsewhere, are included for comparison purposes. Atomic coordinates and thermal parameters and complete bond length and bond angle listings are included in the Supporting Information. The cyclohexane rings in all structures have no significant distortions from the regular chair geometry. The C1–C2 and C1–C6 bond distances in all structures are on average shorter than the remaining C–C bond distances in the cyclohexane rings; this can be rationalized on the basis of hybridization effects caused by the electronegative oxygen substituent at C1; there are no systematic trends in the remaining C–C bond distances. Comparison of the C–O bond distances within the nosylate structures **21-Ns**, **22-Ns**, **23-Ns**, and **32** and the *p*-nitrobenzoates **21-PNB**, **24-PNB**, and **33**, however, do reveal an interesting trend.



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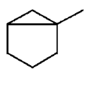

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[25] Zsolnai, L. ZORTEP, *An Interactive ORTEP Program*; University of Heidelberg: Germany, 1994.

Table 1. Selected Bond Distances for the Ester Derivatives 21-Ns, 21-PNB, 22-Ns, 23-Ns, 24-PNB, 32, and 33

				23-Ns				33	
	21-Ns	**21-PNB**	**22-Ns**	**M1***	**M2**	**24-H**	**32**[a]	**M1**[b]	**M2**
C1−O1	1.487(5)	1.459(4)	1.5000(16)	1.498(5)	1.493(5)	1.477(3)	1.487(2)	1.463(2)	1.468(2)
C1−C2	1.519(6)	1.504(6)	1.5130(19)	1.517(6)	1.526(6)	1.515(4)	1.510(2)	1.514(2)	1.512(2)
C2−C3	1.535(6)	1.526(6)	1.5450(19)	1.526(6)	1.532(6)	1.535(4)	1.534(2)	1.529(2)	1.526(2)
C3−C4	1.527(6)	1.580(11)	1.545(2)	1.546(6)	1.545(6)	1.529(4)	1.527(2)	1.537(2)	1.541(2)
C4−C5	1.517(7)	1.488(11)	1.527(2)	1.523(7)	1.537(7)	1.541(4)	1.537(2)	1.536(2)	1.539(2)
C5−C6	1.520(7)	1.521(7)	1.527(2)	1.526(7)	1.528(6)	1.542(4)	1.528(2)	1.535(2)	1.537(2)
C6−C1	1.514(6)	1.496(7)	1.5082(19)	1.514(6)	1.507(6)	1.511(4)	1.511(2)	1.514(2)	1.514(2)
M−C3	2.202(4)	2.178(5)	1.9078(14)	2.173(4)	2.182(4)	2.154(3)			
M−Me (av)	2.140	2.147	1.864	2.147	2.141	2.134			

* There are two molecules in the asymmetric unit: M1 refers to molecule 1 and M2 refers to molecule 2. [a] Reference 26. [b] Reference 13.

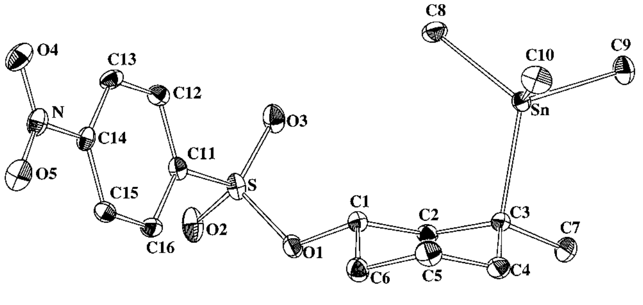


Figure 5. Thermal ellipsoid plot for compound **21-Ns**.

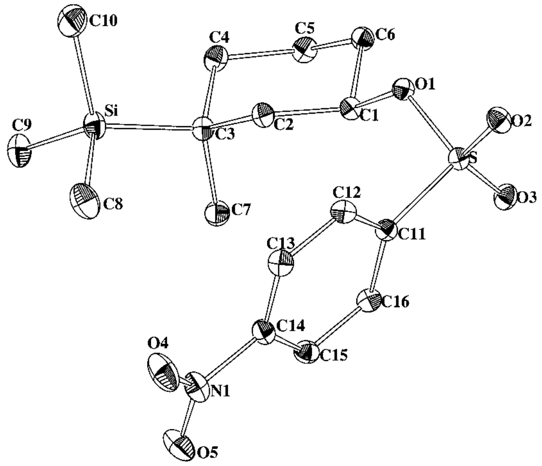


Figure 6. Thermal ellipsoid plot for compound **22-Ns**.

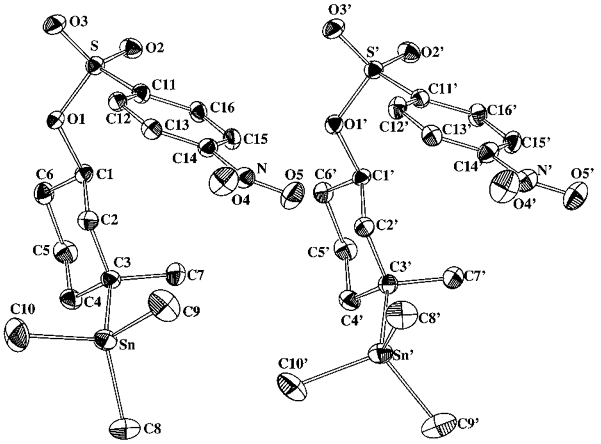


Figure 7. Thermal ellipsoid plot for the two independent molecules of compound **23-Ns**.

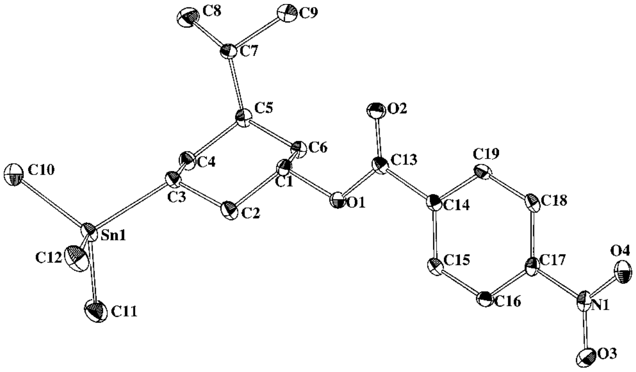


Figure 8. Thermal ellipsoid plot for compound **24-PNB**.

The nosylate **21-Ns** in which the C−Sn bond is axial has a C−O bond distance of 1.487(5) Å, which is identical with that observed for the nonmetalated nosylate derivative **32**, which is 1.487(2) Å, whereas the two independent molecules of the equatorial γ-stannyl nosylate **23-Ns** have C−O bond distances of 1.493(5) and 1.498(5) Å, which appear to be lengthened. The precision with which interatomic distances can be determined in the stannylated ester derivatives is limited due to the presence of the heavy atom in these structures. Thus, although the C−O distances in **23-Ns** appear to be lengthened relative to the axial isomer **21-Ns** and the nonmetalated nosylate **32**, this is only just significant, and these distances have relatively high estimated standard deviation values. The structure of the equatorial γ-silyl nosylate **22-Ns**, however, has a C−O bond distance of 1.500(2) Å, which is more precisely determined and, clearly, significantly lengthened relative to **32**. In all the nosylate structures, the geometry about the sulfonate group is similar, in particular, the S−O1−C1−H1 dihedral angle varies by only 6°; it can be argued, therefore, that any variation in the C−O bond distances in **21-Ns**, **22-Ns**, and both molecules of **23-Ns** is not likely the result of significant differences in nonbonded repulsion. The pattern of C−O bond distances observed for the *p*-nitrobenzoate derivatives **21-PNB**, **24-PNB**, and **33** are similar; the equatorial γ-stannyl *p*-nitrobenzoate structure **24-PNB** (which was well determined) revealed a C−O bond distance of 1.477(3) Å, which is significantly lengthened relative to the nonstannylated ester **33** (1.463(2) and 1.468(2) Å). The axial γ-stannyl *p*-nitrobenzoate **21-PNB** has a C−O bond distance 1.459(4), which does not differ significantly with **33**.

The observation of a slight lengthening of the C−O bond distance in the equatorial γ-silyl **22-Ns** and γ-stannyl **23-Ns**, **24-PNB** esters relative to the nonmetalated esters **32** and **33**, whereas in the axial γ-stannyl esters **21-Ns** and **21-PNB** the C−O bond distances are unaffected, is consistent with the presence of a percaudel

Table 2. Relative Solvolysis Rates for 32, 21-Ns, and 23-Ns in 97% TFE at 0 °C

compd	rel rate
32	1
21-Ns	3.1
23-Ns	$>5.3 \times 10^4$

interaction between the back lobe of the C−M σ bonding orbital and the σ^*_{C-O} antibonding orbital (Figure 3; **18**). This interaction, however, is not possible in the axial stannyl derivatives **21-Ns** and **21-PNB**. The absence of any effects on the C−O bond distances for the axial stannyl derivatives **21-Ns** and **21-PNB** implies that the inductive effect of the metal substituent does not result in any significant enhancement of the $\sigma_{C-C}-\sigma^*_{C-O}$ interaction in the ground state (Figure 3; **19**). This result also suggests that the stabilization of positive charge at the γ-position by silicon and tin is very likely due in most part to the percaudel interaction shown in Figure 1, rather than by inductively enhanced C−C hyperconjugation (Figure 2).

The effects of the equatorial γ-silyl and stannyl substituents on the ground-state structures of the γ-metalated esters **22-Ns**, **23-Ns**, and **24-PNB**, although small, are nonetheless significant. The effects that these substituents have on the solvolytic reactivities of these esters are expected to be much larger, given that the electron demand at an S_N1 (or E1) transition state will be much greater than the electron demand of a σ^*_{C-O} orbital in the ground state. To test this prediction, the solvolytic reactivities of the axial and equatorial γ-stannyl nosylates **21-Ns** and **23-Ns** were determined and compared with the nonmetalated nosylate ester **32**.

Solvolysis Studies

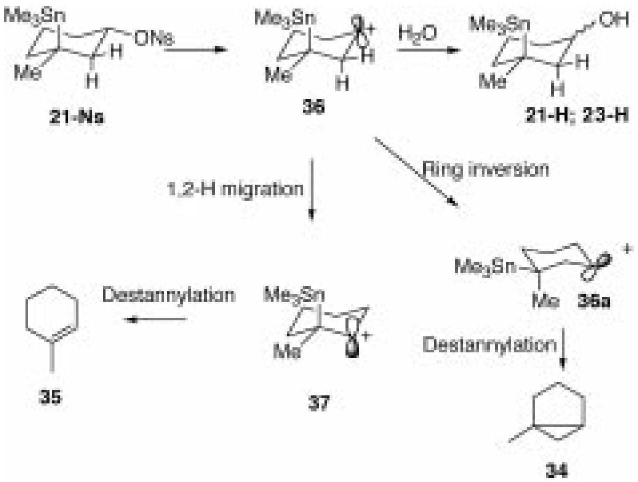
The rates of solvolysis of **21-Ns**, **23-Ns**, and the nonmetalated nosylate derivative **32** were determined in 97% TFE using the NMR method reported by Creary and Jiang.[27] All data used in this study gave reaction rate constants with correlation coefficients of 0.9999 or better. Rates for **21-Ns** and **23-Ns** were measured at various temperatures in order to construct Arrhenius plots that gave the equations (1) and (2) for **32** and **21-Ns**, respectively. The precision of fit for each equation was better than $r = 0.9999$, and these equations were used to predict the rates of solvolysis for **32** and **21-Ns** at 0 °C for comparison purposes (Table 3).

$$\ln k = (-1.18 \times 10^4)(1/T) + 29.23 \qquad (1)$$

$$\ln k = (-1.19 \times 10^4)(1/T) + 30.54 \qquad (2)$$

For **23-Ns**, the solvolysis rate was too fast to be measured accurately even at 0 °C. The first measurement was taken 2 min after solution, and the reaction had already gone to completion. It was conservatively estimated that at least 7 half-lives had passed, meaning that about 99% of the ester had reacted. This gives a minimum rate constant of at least 4.1×10^{-2} s^{-1}, which is more than 50 000 times faster than **32**. Relative rates for **21-Ns**, **23-Ns**, and **32** at 0 °C are presented in Table 3.

Scheme 4



Product Analyses

The three compounds **21-Ns**, **23-Ns**, and **32** were too insoluble in ethanol and in TFE containing more than 10% water for this study. Thus, a more thorough study aimed at determining the molecularity of the reaction could not be carried out. However, the products of solvolysis were easily discernible by ^{1}H NMR analysis of the ca. 0.2 M solutions of each ester in CF_3CD_2OH after more than 10 half-lives. **23-Ns** gave exclusively 1-methylbicyclo[3.1.0]hexane (**34**), for which ^{1}H NMR data had been previously reported.[28] The product resembles the homohyperconjugatively stabilized transition state and is convincing evidence that solvolysis proceeds not via a k_s mechanism but via a k_c mechanism. The major product from solvolysis of the axial γ-tin ester **21-Ns** was 1-methylcyclohexene **35** in 70% yield in addition to small quantities of 1-methylbicyclo[3.1.0]hexane (**34**) (20%) and 3-methyl-3-(trimethylstannyl)cyclohexanol (**21-H**) and (**23-H**) (10%). The formation of these products can be accommodated by the mechanism shown in Scheme 4. Heterolysis of the C−ONs bond in **21-H** results in the formation of the carbenium ion intermediate **36**. A small proportion of this intermediate is captured by water to give 3-methyl-3-(trimethylstannyl)cyclohexanols **21-H** and **23-H**; the major pathway followed, however, is 1,2-hydride migration to give the β-stannyl-stabilized carbenium ion **37**, which then undergoes destannylation to give 1-methylcyclohexene (**35**). This apparently efficient 1,2 H-migration is possibly promoted by the stannyl substituent, which is antiperiplanar to one of the β-hydrogens, possibly imparting some hydridic character by a $\sigma_{C-Sn}-\sigma^*_{C-H}$ interaction. The isolation of 20% 1-methylbicyclo[3.1.0]hexane (**34**) suggests some participation by the γ-stannyl substituent; however, it is unlikely that this participation occurs at the rate-determining step since the activation energies for **21-Ns** (23.63 kcal/mol) and the unsubstituted nosylate **32** (23.52 kcal/mol) are very similar. It is likely that **34** arises from a ring inversion of the initially formed cation **36**, giving the alternative conformer **36a**, which is percaudally stabilized by the γ-stannyl substituent; destannylation of **36a** gives **34**. The major product from solvolysis of tin-free nosylate **32** was 4-*tert*-butylcyclohexene (70%), which was

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(27) Creary, X.; Jiang, Z. *J. Org. Chem.* **1994**, *59*, 5106.

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Table 3. Crystal Data and Structure Refinement Details for Compounds 21-Ns, 21-PNB, 22-Ns, 23-Ns, and 24-PNB

	24-PNB	**21-Ns**	**22-Ns**	**23-Ns**	**21-PNB**
emp formula	$C_{19}H_{29}NO_4Sn$	$C_{16}H_{25}NO_5SSn$	$C_{16}H_{25}NO_5SSi$	$C_{16}H_{25}NO_5SSn$	$C_{17}H_{25}NO_4Sn$
formula wt	454.15	462.12	371.52	462.12	426.07
T (K)	130.0(1)	130.0(1)	130.0(1)	130.0(1)	293(2)
radiatn	Mo Kα	Mo Kα	Cu Kα	Mo Kα	Cu Kα
wavelength (Å)	0.71069	0.71069	1.5418 Å	0.71069	1.5418 Å
cryst system	monoclinic	monoclinic	triclinic	triclinic	triclinic
space grp	$P2_1/c$	$P2_1/c$	P-1	P-1	P-1
unit cell dimens					
a	10.463(2)	6.948(2)	6.4080(10)	12.644(3) Å	7.3775(10)
b	7.235(2)	34.854(10)	10.2900(10)	10.245(3) Å	7.7842(10)
c	29.355(5)	8.526(2)	14.4880(10)	15.117(3)	19.0143(10)
α			95.890(8)	95.49(2)°	81.496(10)
β	109.91(2)	113.15(2)°	96.730(10)	95.07(2)°	83.491(10)
γ			94.460(10)	93.92(2)°	62.008(10)
vol (Å^3)	2089.3(8)	1898.3(9)	939.82(18)	1935.9(8)	952.40(18)
Z	4	4	2	4	2
D_c (Mg/m^3)	1.444	1.617	1.313	1.586	1.486
μ (mm^{-1})	1.244	1.480	2.360	1.451	10.822
F(000)	928	936	396	936	432
cryst size	0.58 × 0.17 × 0.07	0.3 × 0.2 × 0.09	0.35 × 0.1 × 0.07	0.3 × 0.3 × 0.01	0.35 × 0.25 × 0.013
θ range	2.07−25.02	2.34−25.00	3.09−74.95	2.21−30.05	2.35−75.96
index ranges	$0 \leq h \leq 12$	$-8 \leq h \leq 0$	$-7 \leq h \leq 7$	$-17 \leq h \leq 1$	$0 \leq h \leq 9$
	$0 \leq k \leq 8$	$-41 \leq k \leq 9$	$-12 \leq k \leq 12$	$-12 \leq k \leq 12$	$-8 \leq k \leq 9$
	$-32 \leq l \leq 32$	$-9 \leq l \leq 10$	$-18 \leq l \leq 18$	$-17 \leq l \leq 18$	$-23 \leq l \leq 23$
intensity controls	3	3	3	3	3
interval (min)	160	160	160	160	160
decomposition	insignificant	insignificant	insignificant	insignificant	insignificant
absorptn method	analytical	analytical	analytical	analytical	analytical
max min transmission	0.91 and 0.78	0.97 and 0.75	0.86 and 0.67	0.95 and 0.59	0.68 and 0.09
reflns collected	3874	3623	7626	9682	4263
independent	3658	3337	3811	8712	3944
R(int)	0.0144	0.0320	0.0208	0.0541	0.0291
obsd ($I > 2\sigma(I)$)	3173	2728	3577	6907	3370
refinement method	full-matrix on F^2	full-matrix on F^2	full-matrix on F^2	full-matrix on F^2	full-matrix on F^2
data/restraints/param	3657/0/343	3337/0/318	3811/0/318	8712/0/634	3944/0/309
GOF on F^2	1.072	1.144	1.070	1.040	1.035
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0257$	$R_1 = 0.0317$	$R_1 = 0.0315$	$R_1 = 0.0526$	$R_1 = 0.0389$
	$wR_2 = 0.0605$	$wR_2 = 0.0722$	$wR_2 = 0.0832$	$wR_2 = 0.1345$	$wR_2 = 0.1025$
R indices (all data)	$R_1 = 0.0334$	$R_1 = 0.0488$	$R_1 = 0.0336$	$R_1 = 0.0684$	$R_1 = 0.0480$
	$wR_2 = 0.0641$	$wR_2 = 0.0842$	$wR_2 = 0.0847$	$wR_2 = 0.1478$	$R_1 = 0.0480$
weighting scheme					
$w = 1/[\sigma^2(F_o^2) + (A*P)^2 + B*P]$	$A = 0.0287$	$A = 0.0348$	$A = 0.0373$	$A = 0.0946P$	$A = 0.0660$
where $P = (F_o^2 + 2F_c^2)/3$	$B = 2.2534$	$B = 4.3892$	$B = 0.4388$	$B = 3.5366$	$B = 0.6099$
extinction method	SHELXL	SHELXL	SHELXL	SHELXL	SHELXL
extinction coeff	0.0000(2)	0.0000(3)	0.0010(3)	0.0000(3)	0.0019(3)
max shift/esd	0.003	2.081	0.001	0.367	0.362
largest diff peak and hole e Å^{-3}	0.922 and −0.605	1.208 and −1.408	0.621 and −0.324	1.897 and −2.322	1.165 and −0.962

accompanied by small quantities of *cis*- and *trans*-4-*tert*-butylcyclohexanol 10 and 20% yield, respectively.

Conclusion

There is small but significant C−O bond lengthening observed in γ-Si or Sn cyclohexyl esters relative to the corresponding nonmetalated derivatives, provided there exists a W geometrical relationship between the C−M bond and the C−O bond. This result is consistent with the presence of a percaudel interaction between the back lobe of the C−M σ bonding orbital and the C−O σ^* antibonding orbital. The high reactivity of **23-Ns** toward unimolecular solvolysis further demonstrates[29] that small lengthening of C−O bonds can manifest in a decrease in the activation energy for heterolysis of that bond.

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 (130.0 K) for **21-Ns**, **22-Ns**, **23-Ns**, and **24-PNB**. The crystals were flash cooled to 130.0 K using an Oxford Cryostream cooling device. The *p*-nitrobenzoate ester **21-PNB** unfortunately underwent a destructive phase change upon cooling, even when cooled slowly; therefore, data were collected at room temperature. Unit cell dimensions were corrected for any θ zero errors by centering reflections at both positive and negative θ angles. The data were corrected for Lorentz and polarization effects and for absorption (SHELX 76).[30] Structures were solved by direct methods (SHELXS-86)[31] and were refined on F^2 (SHELXL-97).[32] Crystal data and refinement details for **21-Ns**, **21-PNB**, **22-Ns**, **23-Ns**, and **24-PNB** are listed in Table 3.

(b) Synthesis. General experimental details are as reported in a previous paper.[10] Nitrobenzenesulfonyl chloride purchased from Aldrich was purified before use by column chromatography in ether followed by 2-fold recrystallization from chloroform−pentane. 3-Methyl-2-cyclohexenone was purchased from Aldrich, while 5-isopropyl-2-cyclohexenone was prepared by the method of Frank.[33]

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Conjugate Addition of Trimethylstannyllithium to 5-Isopropyl-2-cyclohexenone: Preparation of Ketones 28 and 29. Trimethylstannyl chloride (1.0 M in THF 34.88 mL, 0.142 mol) was added to a mixture of anhydrous tetrahydrofuran (50 mL) and excess lithium metal (10 g) under nitrogen and left stirring overnight. After removal of excess lithium, the reaction mixture was treated with 5-isopropyl-2-cyclohexenone (3.169 g, 0.023 mol), which was added dropwise. After the mixture was stirred for 7 h, water (150 mL) and the mixture were left to stir for 15 min. The resulting mixture was extracted with ether (3 × 75 mL) and the ether solution dried ($MgSO_4$) and then evaporated under reduced pressure to give a mixture of *cis*-5- (**29**) and *trans*-5-isopropyl-3-(trimethylstannyl)cyclohexanone (**28**) in an approximate ratio of 1:4 respectively (6.25 g, 90%). **28:** ^{13}C NMR δ −10.69, 19.79, 20.03, 21.66, 31.01, 31.88, 45.20, 45.30, 45.61, 212.00. **29:** ^{13}C NMR δ −11.74, 19.07, 19.62, 23.53, 32.75, 45.25, 50.16, 212.00.

Sodium Borohydride Reduction of the Isopropyl Ketone Mixture 28 and 29. To an ethanol (100 mL) solution of the crude isomeric mixture of **28** and **29** (3 g, 0.0099 mol) was added sodium borohydride (0.5 g, 0.0132 mol) in portions with stirring at 0 °C. The reaction was left to stir at room temperature for a further 4 h. The reaction mixture was quenched cautiously by adding dilute hydrochloric acid (10 mL) dropwise. Excess water (100 mL) was added, and the mixture was extracted with ether (3 × 50 mL), the combined organic extracts were washed with saturated sodium chloride (2 × 50 mL) and dried, and the solvent was removed under reduced pressure to give an oily residue. In the ^{13}C NMR of this oil, characteristic signals were discernible at δ −11.06 (equatorial $SnMe_3$), 67.35 (C−OH) **24-H**; −9.48 (axial $SnMe_3$), 70.27 (C−OH), **30-H**; −11.92 (equatorial $SnMe_3$), 71.83 (C−OH) **31-H**. The residue (2.4 g 80%) was dissolved in pyridine (10 mL) and stirred on ice under an atmosphere of nitrogen. The mixture was then treated with *p*-nitrobenzoyl chloride (1.6 g, 1.1 equiv) and stirred for 3 h. The resulting slurry was then poured into water (100 mL), and the aqueous suspension was extracted with ether (3 × 50 mL). The combined extracts washed with 1 M HCl (3 × 50 mL) and aqueous $NaaHCO_3$ (10%, 3 × 50 mL), dried ($MgSO_4$), and evaporated down to a creamy solid (4 g 90%). The mixture of *p*-nitrobenzoates **24-PNB**, **30-PNB**, and **31-PNB** was partially separated by dry flash chromatography on silica gel using ether/petroleum ether as eluants. Partially purified fractions were repeatedly recrystallized from methanol to afford *r*-5-isopropyl-*t*-3-(trimethylstannyl)cyclohexan-*t*-1-yl *p*-nitrobenzoate (**24-PNB**) as yellow needlelike crystals (300 mg): mp 95−97.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.3 (1H, d, $J = 9$ Hz), 8.3 (1H, d, $J = 9$ Hz), 5.05 (1H, m), 2.2−2.0 (2H, m), 1.95−1.75 (2H, m), 1.5−1.1 (5H, m), 0.9 (3H, d $J = 6$ Hz); ^{13}C NMR δ −11.52, 16.74, 21.09, 21.16, 26.86, 31.56, 34.19, 35.79, 42.27, 73.05, 123.36, 130.57, 136.31, 150.36, 164.21.

The ester **24-PNB** (200 mg) was refluxed in methanol (20 mL) containing potassium hydroxide (2 equiv) for 2 h. The solution was diluted with water (100 mL) and extracted with ether (3 × 50 mL), and the combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure, giving *r*-5-isopropyl-*t*-3-(trimethylstannyl)cyclohexan-*t*-1-ol (**24-H**) (120 mg, 90%): ^{13}C NMR ($CDCl_3$) δ −11.06, 17.8, 20.80 (overlapping *i*-Pr CH_3's), 27.97, 31.93, 37.65, 38.98, 41.03, 67.35.

3-Methyl-3-(trimethylsilyl)cyclohexanone (25). A solution of HMPA (30 mL) and hexamethyldisilane (8.9 mL, 0.044 mol) was cooled with stirring to 0 °C. The mixture was then diluted with cold THF (15 mL at −78 °C) and treated immediately with methyllithium (1.4 mol solution in ether, 25 mL) followed by the addition of cold THF (100 mL, −70 °C). The resulting bright red mixture was cooled to −78 °C and treated with a solution of 3-methylcyclohexanone (3.01 g, 0.027 mol) in THF (5 mL). The mixture was stirred at −78 °C for a further 15 min, warmed to room temperature, and stirred for a further hour. The addition of methanol (15 mL) was followed by extraction with petroleum (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL) and brine (3 × 50 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give **25** as a colorless oil (2.904 g, 58%), which was contaminated by a small amount (ca. 10%) of 3-(pentamethyldisilanyl)-3-methylcyclohexanone (**26**). Purification by silica gel column chromatography gave **25** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.32 (1H, d, $J = 12.6$ Hz, $H2_{ax}$), 2.28−2.24 (2H, m, $H6_{ax,eq}$), 2.06−1.92 (3H, m, $H2_{eq}$, $H5_{ax,eq}$), 1.74 (1H, ddd, $J = 14.2$, 12.6, 4.7 Hz, $H4_{ax}$), 1.52−1.44 (1H, m, $H4_{eq}$), 0.89 (3H, s), −0.05 (9H, s); ^{13}C NMR ($CDCl_3$) δ 212.58 (C1), 47.88 (C2), 41.32 (C6), 30.50 (C4), 25.55 (C3), 22.79 (C5), 18.58 (Me), −4.99 (SiMe's). Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93. Found: C, 64.95; H, 10.84.

3-Methyl-3-(trimethylstannyl)cyclohexanone (27). A solution of trimethylstannyl chloride (0.014 mol in THF 23.5 mL) was treated with lithium metal (0.09 mol) and sonicated for 3 h. The excess lithium was removed, and the resulting cloudy green solution was cooled to 0 °C, treated with a solution of 3-methyl-2-cyclohexanone (1 g, 0.009 mol, in THF 5 mL), and stirred at room temperature for 12 h. The resulting mixture was diluted with water (50 mL) and extracted with ether (5 × 30 mL). The combined ether extracts were washed with water (3 × 100 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give **27** as an oil (2.4 g, 90%) that was pure by ^{13}C NMR. An analytically pure sample was prepared by Kugelrohr distillation (90° C, 0.4 mmHg): ^{1}H NMR ($CDCl_3$) δ 2.53 (1H, d, $J = 15.2$ Hz, $H2_{ax}$), 2.38−2.2 (2H, m, $H6_{ax,eq}$), 2.16 (1H, dd, $J = 15.2$, 2.6 Hz, $H2_{eq}$), 2.07 (1H, m, H5), 1.97 (1H, m, $H4_{eq}$), 1.74 (1H, m, H5), 1.57 (1H, ddd, $J = 16.0$, 10.0, 5.0 Hz, $H4_{ax}$), 1.15, (3H, s), 0.02, (9H, s); ^{13}C NMR ($CDCl_3$) δ 211.5 (C1), 53.73 (C2), 41.30 (C6), 37.04 (C5), 31.32 (C3), 26.37 (Me), 24.73 (C4), −11.03; MS M^+ 276.0526 (calcd for $C_{10}H_{20}OSn$ 276.0536); IR ν_{max} (thin film) 1707, 767 cm^{-1}.

***trans*-3-Methyl-3-(trimethylsilyl)cyclohexanol (20-H).** A solution of L-Selectride (0.001 mol) in anhydrous THF (10 mL), stirred under nitrogen, was cooled to −78 °C and treated with a solution of 3-methyl-3-(trimethylsilyl)cyclohexanone (**25**) (0.20 g, 0.001 mol). The resulting mixture was stirred at this temperature for 4 h and then quenched by the addition of water (3 mL) and allowed to reach room temperature. The resulting solution was treated with with sodium hydroxide (3 M, 0.24 mL) and 30% H_2O_2 (dropwise) and stirred for 1 h. The mixture was extracted with ether (3 × 50 mL), and the combined extracts were washed with brine (3 × 50 mL), dried ($MgSO_4$), and evaporated to give **20** as a colorless oil (0.15 g, 73%): ^{13}C NMR ($CDCl_3$) δ 68.11, 44.50, 35.00, 34.96, 26.59, 20.87, 18.98, −2.24; IR ν_{max} (thin film) 3454, 1068 cm^{-1}.

***trans*-3-Methyl-3-(trimethylstannyl)cyclohexanol (21-H).** A solution of L-Selectride (0.0018 mol) in anhydrous THF (10 mL) was cooled to −78 °C and then treated with a solution of 3-methyl-3-(trimethylstannyl)cyclohexanone (**27**) in THF (5 mL). The resulting mixture was stirred at this temperature for 4 h and then diluted with water (3 mL) and allowed to reach room temperature. Treatment with aqueous sodium hydroxide (3M, 0.6 mL) was followed by dropwise addition of 30% H_2O_2 (0.6 mL). The mixture was stirred for a further hour and then extracted with ether (3 × 50 mL). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give **21** as a colorless oil: ^{13}C ($CDCl_3$) δ 69.21, 49.47, 38.94, 35.46, 31.16, 29.27, 23.86, −9.69; IR ν_{max} (thin film) 3345, 1447 cm^{-1}.

***cis*-3-Methyl-3-(trimethylstannyl)cyclohexanol (23-H).** A stirred solution of 3-methyl-3-(trimethylstannyl)cyclohexanone (**27**) (0.51 g, 0.0019 mol) in ethanol (50 mL), was treated at 0 °C with sodium borohydride (0.14 g, 0.004 mol). The resulting mixture was stirred at this temperature for 4 h and then quenched by the addition of 1 M HCl (5 mL). The resulting mixture was extracted with ether (3 × 50 mL), and the combined extracts were washed with brine (3 × 50 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give **21-H** and **23-H** as a ca. 1:1 mixture (0.42 g, 84%). Separation by flash chromatography on silica gel with ether/petroleum eluants gave **21-H** and *cis*-3-methyl-3-(trimethylstannyl)cyclohexanol (**23-H**): ^{13}C NMR ($CDCl_3$) δ 66.00, 45.38, 35.90, 35.70, 25.93, 23.50, 19.69, −11.63; IR ν_{max} (thin film) 3357, 1447, 1048, 762 cm^{-1}.

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***cis*-3-Methyl-3-(trimethylsilyl)cyclohexanol (22-H).** A mixture of 3-methyl-3-(trimethylsilyl)cyclohexanone (**25**) (0.53 g, 0.0028 mol), water (0.3 mL), and ether (25 mL) was stirred at 0 °C. The mixture was then treated with sodium metal (0.29 g, 0.0127 mol) and left to stir at 0 °C for 4 h. Ethanol (1 mL) was added to destroy the excess sodium, and then water (10 mL) was added. The organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure to give **22-H** as a colorless oil (0.33 g, 65%): ^{13}C NMR ($CDCl_3$) δ 66.02, 40.75, 36.23, 30.21, 21.23, 19.64, 17.89, −5.26.

***trans*-3-Methyl-3-(trimethylstannyl)cyclohexyl *p*-Nitrobenzoate (21-PNB).** A stirred mixture of *p*-nitrobenzoyl chloride (0.206 g, 0.0011 mol) and pyridine (0.5 mL), was treated at 0 °C with a solution of *trans*-3-methyl-3-(trimethylstannyl)cyclohexanol (**21-H**) (0.200 g, 0.0007 mol) in pyridine (0.75 mL). The resulting mixture was stirred at room temperature for 1 h and cooled to 0 °C, and excess *p*-nitrobenzoyl chloride was quenched by the addition of water (0.5 mL). The mixture was stirred for 20 min and then extracted with ether (3 × 50 mL), washed with 10% $CuSO_4$ solution (2 × 50 mL), water (50 mL), and then aqueous $NaHCO_3$ (10%, 2 × 50 mL), dried ($MgSO_4$), and evaporated down to a solid. Crystallization from ether/ petroleum yielded **21-H** as clear plates (0.18 g, 60%): mp 107.5−108.5 °C; ^1H NMR ($CDCl_3$) δ 8.26 (2H, d, J = 9 Hz), 8.18 (2H, d, J = 9 Hz), 5.06 (1H, m), 2.26 (1H, m), 2.08 (1H, m), 1.84 (2H, m), 1.56−1.18 (4H, m), 1.16 (3H, s), 0.14 (9H, s); ^{13}C NMR ($CDCl_3$) δ 164.08, 130.61, 123.44, 74.02, 45.22, 38.84, 31.60, 30.72, 29.23, 23.57, −9.74.

General Procedure for the Preparation of *p*-Nitrobenzenesulfonate Derivatives 20-Ns, 21-Ns, 22-Ns, and 23-Ns. Nitrobenzenesulfonyl chloride (1.2 equiv) was dissolved in pyridine (freshly distilled, 0.5 mL) at 0 °C under an atmosphere of nitrogen as the alcohol (0.1 g) was added all at once. The reaction was stirred at this temperature for 1 h and left at 0 °C overnight. The reaction was diluted with cold diethyl ether (freshly distilled; 30 mL) and filtered into a separation flask. The solution was washed with cold cupric sulfate solution (saturated; 3 × 10 mL) followed by cold sodium bicarbonate (2 × 10 mL) before it was dried with magnesium sulfate. Filtration and concentration (in vacuo) gave solids that could usually be purified by radial chromatography and crystallization; however, the nosylates were generally susceptible to decomposition after a short exposure to the atmosphere, so these esters were stored and handled, as far as possible, under nitrogen.

***trans*-3-Methyl-3-(trimethylsilyl)cyclohexyl nosylate (20-Ns):** colorless powder from pentane (80%); mp 95−96 °C; ^1H NMR ($CDCl_3$) δ 8.39 (2H, d, J = 8 Hz), 8.04 (2H, d, J = 8 Hz), 4.8 (1H, m), 1.5−1.9 (5H, m), 1.4−1.0 (3H, m), 0.92 (3H, s), −0.12 (9H, s); ^{13}C NMR ($CDCl_3$) δ −3.34, 18.66, 21.59, 24.06, 31.65, 32.90, 39.41, 82.25, 124.29, 128.84, 143.2, 150.4.

***trans*-3-Methyl-3-(trimethylstannyl)cyclohexyl nosylate (21-Ns):** colorless blocks from pentane in 90% yield; mp 71−72 °C; ^1H NMR δ 0.01 (s, 9H), 1.08 (s, 3H), 1.2−1.4 (m, 4H), 1.7−1.8 (m, 2H), 1.93 (br d, J = 12 Hz, 1H), 2.10 (d, J = 12 Hz, 1H), 4.57 (septet, J = 5 Hz, 1H), 8.23 (ab quartet, 4H); ^{13}C δ −9.84, 23.56, 28.98, 30.82, 32.41, 38.16, 45.97, 82.81, 124.36, 128.93, 143.39, 150.52

***cis*-3-Methyl-3-(trimethylsilyl)cyclohexyl nosylate (22-Ns):** colorless needles from pentane (85%); mp 92−93 °C; ^1H NMR ($CDCl_3$) δ 8.4 (2H, d, J = 8 Hz), 8.05 (2H, d, J = 8 Hz), 4.9 (1H, m), 1.95 (1H, m), 1.5−1.9 (3H, m), 1.2−1.5 (4H, m), 0.95 (3H, s), −1.4 (9H, s); ^{13}C NMR ($CDCl_3$) δ 150.41, 143.25, 128.68, 124.88, 81.99, 37.98, 33.10, 29.47, 22.01, 19.60, 17.41, −5.45.

***cis*-3-Methyl-3-(trimethylstannyl)cyclohexyl nosylate (23-Ns):** colorless blocks from pentane; 87% yield; mp 230−236 °C dec; ^1H NMR δ 0.00 (9H, s), 1.12 (3H, s), 1.2−1.9 (m, 8H), 4.88 (septet, J = 3.5 Hz, 1H), 8.22 (ab quartet, 4H); ^{13}C δ −11.55, 19.69, 23.69, 25.74, 32.60, 35.20, 42.59, 81.52, 124.33, 128.90, 143.38, 150.2.

Kinetics. Solvents for the kinetics experiments were purified as follows. 2,6-Lutidine was stirred over KOH for 24 h before distillation from CaH_2 under nitrogen. Trifluoroethanol was stirred over sodium sulfate for 10 min and then over sodium bicarbonate for 10 min followed by distillation under nitrogen, distilled, and stored under an atmosphere of nitrogen and over 4 Å molecular sieves.

The method used was based on that reported by Creary and Jiang.[27] The substrate (1.5×10^{-5} mol) was dissolved in 0.5 mL of a solution of 0.04 M 2,6-lutidine in 97% trifluoroethanol. The solution was added to an NMR tube that contained an insert tube of acetone-d_6 as a standard and locking signal. The NMR tube was kept in the temperature-controlled probe and periodically analyzed so that 30−40 measurements were obtained over approximately 2 half-lives. An infinity reading was taken after at least 10 half-lives.

Product Determination. The substrate (1.0×10^{-4} mol) was dissolved in 0.5 mL of a solution of 0.25 M 2,6-lutidine in 97% trifluoroethanol. The solution was added to an NMR tube and sealed. After at least 10 half-lives, the solution was analyzed by ^1H NMR, which showed the resonances reported below.

23-Ns: 1-methylbicyclo[3.1.0]hexane;[28] δ 0.17 (dd, J = 8.1, 4.5 Hz, 1H, CH_2 of cyclopropane ring), 0.33 (t, J = 4.5 Hz, 1H, CH_2 of cyclopropane ring), 0.52 (s, 9H, Me_3SnOR), 0.91 (quintet, J = 4 Hz, 1H, bridgehead CH), 1.20 (s, 3H, Me), 1.48−1.83 (m, 6H, 3 × CH_2 of cyclopentane ring);

21-Ns: δ 0.47 (s, 9H, Me_3SnOR, corresponds to the formation of both 1-methylbicyclo[3.1.0]hexane and 1-methylcyclohexene); 1-methylcyclohexene (70%) 1.46−1.64 (m incorporating singlet at 1.6, 7H, Me and ring CH_2), 1.84−1.97 (m, 4H), 5.35−5.40 (m, 1H, olefin CH); 1-methylbicyclo[3.1.0]hexane (20%, signals as from solvolysis of **23-Ns**); *trans*-3-methyl-3-trimethylstannylcyclohexanol (10%) δ −0.01 (s, 9H), 1.1 (s, 3H).

32: 4-*tert*-butylcyclohexene (90%), δ 0.86 (s, 9H, *tert*-butyl CH_3), 1.1−1.35 (m, 1H, ring CH), 1.7−2.2 (m, 6H, ring CH_2), 5.68 (s, 2H, olefinic CH); *cis*-4-*tert*-butylcyclohexanol (ca. 20%) 4.05 (br s, 1H); *trans*-4-*tert*-butylcyclohexanol (10%), 3.75 (m, 1H, CHOH).

Acknowledgment. Our thanks go to the Australian Research Council Large Grants Scheme for financial support and to Dr. John Lawlor of this department for helpful criticisms in the preparation of this manuscript.

Supporting Information Available: Solvolysis data for **37** and **42**, spectral data for **37** and **39**, and a full listing of bond distances, angles, dihedral angles, anisotropic displacement parameters and H atom coordinates for **21-PNB**, **21-Ns**, **22-Ns**, **23-Ns**, and **24-PNB** (52 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.

JO9723265