

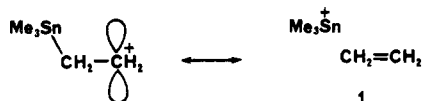
The ζ (Zeta) Effect of TinJoseph B. Lambert,^{*1} Lourdes A. Salvador, and Charlotte L. Stern

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cis,trans,cis-6-(Trimethylstannyl)-2-decalyl tosylate (5-OTs) was prepared in order to test whether tin can assist in the formation of a carbocation over six bonds (a ζ effect). This system has the requisite diequatorial (zigzag) arrangement of nucleofuge and electrofuge to give rise to triple hyperconjugation. Comparisons were made with the axial-equatorial *trans,trans,cis* isomer (6-OTs) and with the analogous equatorial and axial decalin systems lacking the tin group (7-OTs and 8-OTs). The diequatorial system 5-OTs did not show a rate acceleration in comparison with the models, and its rate was sensitive to solvent nucleophilicity. Products for both 5 and 6 were substitution with inversion and elimination. These observations indicate that tin does not assist in positive charge development over six bonds.

The group IV (14) elements below carbon exhibit a remarkable ability to stabilize positive charge on adjacent carbon atoms through hyperconjugation (σ - π conjugation). The β effect of silicon² is probably the best known example of this phenomenon, although the β effects of germanium and, particularly, tin are even larger.³ Structure 1 illustrates this phenomenon for tin. The gamma effects of

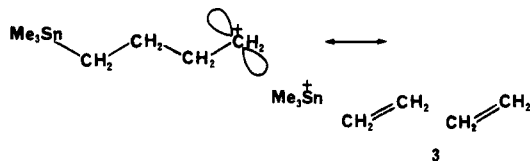


silicon and tin are considerably weaker than their respective β effects,^{2,4-7} as they are based on homohyperconjugation (2). Again the γ effect is stronger for tin, which is



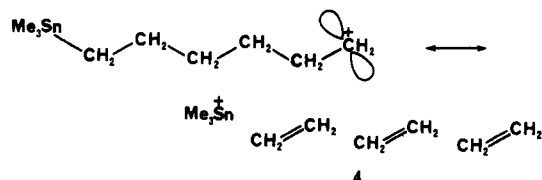
more electropositive and more polarizable than silicon and hence is better able to stabilize positive charge through the mechanisms illustrated by 1 and 2.

A δ effect would involve delocalization over four bonds, as illustrated by 3, and has been attributed to double or second-sphere hyperconjugation. Modest δ effects of

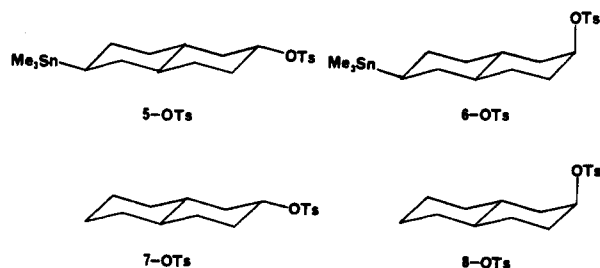


silicon and germanium have been documented,⁸ but much larger effects have been demonstrated when tin is the donor atom.^{5,8,9}

If the concept of σ delocalization through multiple hyperconjugation is carried to the next stages, one could imagine double homohyperconjugation over five bonds (an ϵ effect) or triple hyperconjugation over six bonds (a ζ (zeta) effect). In an attempt to define the limits of σ delocalization, we have explored the possible existence of triple hyperconjugation using tin as the donor atom, as its effects have been observed to be larger than those of silicon or germanium for all comparable cases studied. To optimize the effect, a structure was needed that contains a series of antiperiplanar (zigzag) interactions over six bonds, as in 4. For the cases of the β effect of silicon² and



the δ effect of tin,^{8,9} elimination of conformational mobility about the intervening bonds heightened the interaction, possibly both through a more favorable conformer population and through tighter geometries. Consequently, we selected the rigid decalin framework for our study of charge delocalization over six bonds (4). The optimal, zigzag geometry is found in the *trans* system 5. Useful comparisons are the analogous *cis* geometry 6 and the



decalin rings with similarly disposed leaving groups but lacking tin (7, 8). We have prepared these four systems

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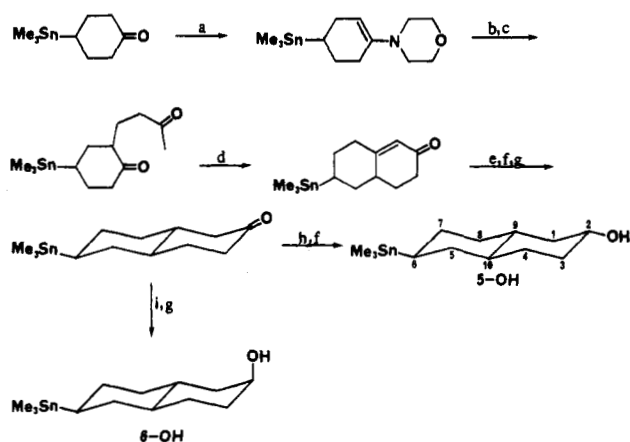
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Scheme I^a

^a (a) Morpholine, toluene, reflux; (b) MVK, dioxane; (c) H₂O; (d) cat. pyrrolidine, benzene, reflux; (e) Li, NH₃, -78 °C; (f) column chromatography; (g) recrystallization; (h) LiAlH₄; (i) KBH(sec-Bu)₃.

and report herein on a search for triple hyperconjugation through a ζ effect of tin.

Results

A synthesis of 5, the test substrate for a ζ effect of tin, had to control placement of two equatorial groups within a trans-fused decalin ring. The trans fusion can be achieved through dissolved metal reduction of $\Delta^{1,9}$ -2-octalone,¹⁰ and suitable hydride reduction of that ketone should be able to lead to either an equatorial (5) or an axial (6) alcohol. The unsaturated decalone in turn can be produced by an aldol-type condensation. This strategy led to the successful synthesis of the alcohol derivatives for 5 and 6, as illustrated in Scheme I.

The starting material, 4-(trimethylstannyl)cyclohexanone, was available from our previous study of the δ effect of tin.^{5,9} Enamine alkylation was chosen over base-catalyzed alkylation to avoid cleavage of the C-Sn bond. The morpholino enamine of cyclohexanone was known to react with methyl vinyl ketone, and the resulting alkylation product spontaneously cyclizes.¹¹ The stannyl diketone of Scheme I yielded under similar conditions only partial cyclization, so that an additional basic step was necessary to complete ring closure. The decalone then was converted by reduction with lithium aluminum hydride to the cis-, trans-, cis isomer ("cis" and "trans" express the relationship between the tertiary ring hydrogens), which we will call the *trans*-alcohol, 5-OH. Reduction with potassium tri-*sec*-butyl borohydride yielded the trans,trans,cis isomer (the enumeration begins with the hydrogen geminal to tosylate), which we will refer to as the *cis*-alcohol, 6-OH.

The two isomers were easily distinguished by the resonance of the proton geminal to hydroxyl. The axial resonance for the equatorial alcohol appears at higher field than the equatorial resonance for the axial alcohol (δ 3.57 vs 4.07). Splitting of the axial proton by two adjacent axial protons is clearly visible as a triplet of quartets for the equatorial alcohol, whereas the resonance of the equatorial proton in the axial alcohol is a broad singlet.

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Table I. Rate Measurements

system	geometry of OTs	solvent ^a	temp, °C	r^{2b}	rate, s ⁻¹
5-OTs	equatorial	97% TFE	75.0	0.9999	4.23×10^{-4}
			50.0	0.9999	2.90×10^{-5}
		80% TFE	25.0		1.26×10^{-6} ^c
			75.0	0.9999	6.42×10^{-4}
			75.0	0.9999	1.24×10^{-3}
			75.0	0.9999	1.09×10^{-4}
6-OTs	axial	97% TFE	75.0	0.9999	1.30×10^{-4}
			50.0	0.9999	2.44×10^{-4}
		80% TFE	75.0	0.9998	1.04×10^{-3}
			25.0		8.40×10^{-5} ^c
			75.0	0.9999	4.41×10^{-6} ^c
			75.0	0.9999	2.28×10^{-3}
7-OTs	equatorial	97% TFE	75.0	0.9999	3.70×10^{-3}
			75.0	0.9999	2.22×10^{-4}
			75.0	0.9999	5.28×10^{-4}
8-OTs	axial	97% TFE	75.0	0.9999	6.30×10^{-4}
			75.0	0.9996	2.82×10^{-4}
			75.0	0.9996	7.97×10^{-4}

^a TFE in trifluoroethanol (w/w%); ethanol values are v/v%.

^b Square of correlation coefficient; mean for two runs. ^c Extrapolated from values at higher temperatures.

Assignment of the carbon resonances was facilitated by the tin satellites. The large $^1J(^{117,119}\text{Sn}-^1\text{H})$ coupling gives rise to a pair of peaks on either side of the resonance of C6 (see Scheme I for the substituent-independent decalin numbering system), separated by some 395 Hz. Carbons 5 and 7 are geminal to tin and give a 2J of only 15-20 Hz, leading to tin satellites barely separated from the base of the centerband. Carbons 8 and 10 are vicinal to tin and give a 3J of about 60 Hz, leading to satellites clearly separated from but close to the centerbands. The attached proton test distinguished the four methinyl carbons (2, 6, 9, 10) from the six methylene carbons (1, 3, 4, 5, 7, 8). Known chemical shift trends in the nonstannylated *trans*-2-decalols were used to assign the remaining carbons.

As there was no certainty that the ring juncture was *trans*, we had recourse to X-ray crystallography of 5-OTs to confirm the structure. The deductions from the NMR spectra were confirmed.

The alcohols were converted by the Tipson procedure to the tosylates for conductometric measurements of rates.¹² This leaving group was chosen because it has good ionizing properties and because for these systems the rates were measurable in a convenient temperature range. Rates were determined in aqueous mixtures of ethanol and trifluoroethanol (TFE) (Table I). From the variation of the rates with temperature, the following activation parameters were calculated: for the *trans* system (5-OTs) $\Delta H^\ddagger = 23.4$ kcal mol⁻¹, $\Delta S^\ddagger = -7.1$ eu, $\Delta G^\ddagger = 25.5$ kcal mol⁻¹; for the *cis* system (6-OTs) $\Delta H^\ddagger = 21.9$ kcal mol⁻¹, $\Delta S^\ddagger = -9.5$ eu, $\Delta G^\ddagger = 24.7$ kcal mol⁻¹.

Products were determined in 80% ethanol at 75 °C. For the *trans*-tosylate (5-OTs, with equatorial OTs) in ethanol there were 56% alkenes and 40% inverted substitution product. The substitution component consisted of 24% *trans,trans,cis*-6-(trimethylstannyl)-2-decalol (6-OH, with axial OH) and 16% ethyl *trans,trans,cis*-6-(trimethylstannyl)-2-decalyl ether (6-OEt, with axial OEt). The NMR spectra identified the alkene products to be 6-(trimethylstannyl)-*trans*- $\Delta^{2,3}$ -octalin (37%) and 6-(trimethylstannyl)-*trans*- $\Delta^{1,2}$ -octalin (19%). For the *cis*-tosylate (6-OTs, with the axial OTs), the products in ethanol consisted of 42% of 6-(trimethylstannyl)-*trans*-

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$\Delta^{2,3}$ -octalin, 22% of 6-(trimethylstannyl)-*trans*- $\Delta^{1,2}$ -octalin, 8% of the inverted *cis,trans,cis*-6-(trimethylstannyl)-2-decalol (5-OH, with equatorial OH), and 6% of the inverted ethyl *cis,trans,cis*-6-(trimethylstannyl)-2-decalyl ether (5-OEt, with equatorial OEt).

Discussion

In contrast to their β , γ , and δ counterparts, the ζ effect systems do not exhibit rate enhancements. We compared the ζ -tin equatorial system, 5-OTs, which has the proper geometry for triple hyperconjugative overlap, with the analogous tin-free decalin system 7-OTs. The 5/7 rate ratio is 1.5 in 97% TFE at 75 °C, as there is little or no acceleration by tin. The ζ -tin axial system 6-OTs, which has a skew geometry between Sn and OTs that would provide poor orbital overlap, has essentially the same rate in comparison with the tin-free axial decalin tosylate, 6/8 = 1.3. The trimethyltin group may impart a small geometry change in the ground state that is responsible for the slight acceleration in both systems. Within the pair of tin-containing substrates, triple hyperconjugation in 5 should impart a rate acceleration with respect to 6, but in reality 5 solvolyzes more slowly than 6 in 97% TFE at 75 °C, 6/5 = 2.4. This ratio is typical for a comparison of structurally analogous axial and equatorial systems.¹³ The slightly faster rate of the axial isomer is usually attributed to relief of steric strain or to more favorable solvation. Thus the trimethyltin group has no significant influence on the rate of departure of the ζ tosylate.

We have found that variation of solvent ionizing power and nucleophilicity sometimes can detect incipient orbital overlap even in the absence of a clear rate acceleration.¹⁴ Consequently, we measured the rates of 5-OTs and 6-OTs in the range of solvents listed in Table I. In TFE mixtures, increasing the water concentration produces an increase in nucleophilicity without palpably changing the ionizing power. In ethanol mixtures, increasing the water concentration produces an increase in ionizing power with little change in nucleophilicity. When the reaction rates in these solvent mixtures are plotted vs those of 1-adamantyl bromide, which reacts via a carbocation intermediate (a k_c mechanism), a single straight line is obtained for another k_c substrate.¹⁵ Molecules that react via solvent intervention (k_s , which includes S_N2 , E2, or other mechanisms that have a molecule of solvent in the transition state) produce two distinct lines for the TFE and ethanol data when plotted vs 1-adamantyl bromide.¹⁵ In cases with a change in mechanism between TFE and ethanol, a single curved line can be obtained.

The Raber-Harris plots for 5-OTs and 6-OTs are nearly identical, and are best described as containing two lines (Figures 1 and 2). For the axial isomer 6-OTs (Figure 2), the ethanol line has a slope of 0.26 ($r^2 = 0.99$) and the TFE line has a slope of 2.03 ($r^2 = 0.98$). The r^2 for a single line encompassing all points would drop to 0.87. The difference in the slopes of the two separate lines indicates high

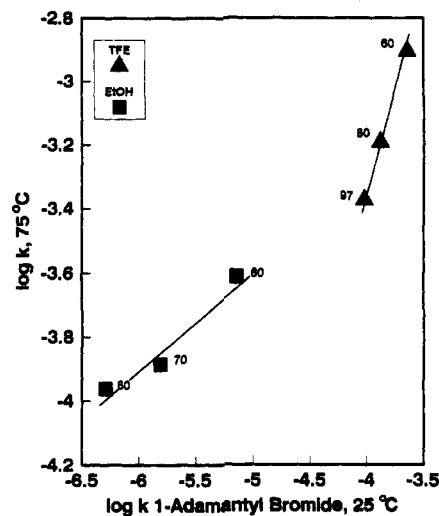


Figure 1. Raber-Harris plot for *cis,trans,cis*-6-(trimethylstannyl)-2-decalyl tosylate (5-OTs) at 75 °C.

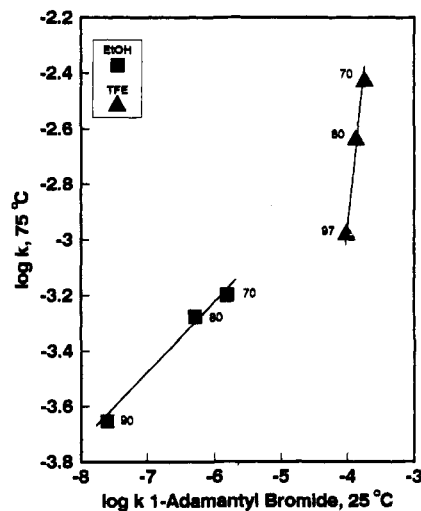
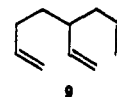


Figure 2. Raber-Harris plot for *trans,trans,cis*-6-(trimethylstannyl)-2-decalyl tosylate (6-OTs) at 75 °C.

sensitivity to nucleophilicity and low sensitivity to ionizing power. There are slight changes for the equatorial isomer 5-OTs (Figure 1). The ethanol line has a slope of 0.31 ($r^2 = 0.95$) and the TFE line a slope of 1.22 ($r^2 = 0.99$), and the combined r^2 is 0.93. The rate is more sensitive to nucleophilicity than to ionizing power, but the sensitivity to nucleophilicity has clearly dropped in comparison with 6-OTs. Thus there is a hint, but only a hint, of triple conjugation in the trifluoroethanol solvolysis of 5-OTs.

Product analysis in 80% ethanol was entirely consistent with a solvent assistance (k_s) mechanism, as the predominant products for both 5-OTs and 6-OTs come from substitution with inversion and elimination. We particularly looked for 4-vinyl-1,7-octadiene (9) in the product mixtures from all solvents, as this is the structure that



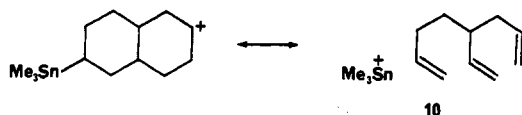
resembles the triple hyperconjugation valence structure (10). In the cases of the γ and δ systems, fragmentation products were observed that resembled the canonical structures representing homohyperconjugation and double

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hyperconjugation, respectively. We found no trace of 4-vinyl-1,7-octadiene in the ζ systems.

Conclusions

The presence of a trimethylstannyl group ζ to tosylate along a zigzag pathway of C–C bonds does not enhance the rate of departure of the leaving group (5-OTs), in comparison with systems that lack tin (7-OTs and 8-OTs) or with one with tin in a nonzigzag pathway (6-OTs). Moreover, the rate of the zigzag system is sensitive to solvent nucleophilicity and is poorly sensitive to ionizing power, although to a slightly smaller extent than is the nonzigzag system. The products in both cases in aqueous ethanol are primarily substitution with inversion and elimination. We conclude that over six bonds, even when held in the most favorable steric orientation by the rigid *trans*-decalin skeleton, the tin atom has little or no ability under these conditions to accelerate formation of a carbocation. The ability of tin to stabilize a remote positive charge has reached its limit.

Experimental Section

4-(Trimethylstannyl)cyclohexanone. According to the procedure of Corey and Suggs,¹⁶ 4-(trimethylstannyl)cyclohexanol⁶ (40.13 g, 0.153 mol) in 60 mL of freshly distilled CH_2Cl_2 was added in one portion with vigorous stirring to a mixture of excess pyridinium chlorochromate (49.57 g, 0.230 mol, 1.5 equiv) in 300 mL of CH_2Cl_2 at room temperature. The mixture was stirred for 4 h and then was allowed to stand overnight. Diethyl ether (300 mL) was added, and the liquid was decanted from the black, tarry residue. This process was repeated three times with 100-mL portions of ether. Vacuum filtration of the ethereal extracts through a mat of Florisil gave a clear green solution, which became a yellow oil with a green precipitate upon evaporation of solvent. The crude product was filtered, and the precipitate was rinsed with hexane to ensure full recovery of the oil. Hexane was removed by rotary evaporation, and the crude oil was distilled under reduced pressure to give 35.67 g of a colorless oil (bp 78–85 °C (0.2 mmHg)), which solidified on cooling. Recrystallization from hexane gave 28.29 g (72%, mp 38–39 °C) of white crystals: ^1H NMR (CDCl_3) δ 0.05 (s, 9H ($^2J_{\text{SnH}} = 52.0, 50.0$ Hz), Me_3Sn), 1.42 (t of t, 1H, SnCH), 1.71 (q of d, 2H, ring), 2.15–2.35 (m, 4H, ring), 2.35–2.45 (m, 2H, ring); ^{13}C NMR (CDCl_3) δ -11.46 (Me_3Sn), $^1J_{\text{SnC}} = 304$ Hz), 23.39 (C4), 31.96 (C3), 44.37 (C2, $^3J = 63.3$ Hz), 212.26 (C1); ^{119}Sn NMR (CDCl_3) δ 5.43.

1-Morpholino-4-(trimethylstannyl)cyclohexene. The procedure was derived from the preparation of 1-morpholino-1-cyclohexene.¹¹ A solution of 4-(trimethylstannyl)cyclohexanone (6.52 g, 0.025 mol), morpholine (2.7 mL, 0.03 mol), and about 0.02 g of tosic acid monohydrate in 30 mL of toluene was heated to boiling for 24 h in a round-bottomed flask equipped with a water separator and a reflux condenser. Toluene was removed by distillation at atmospheric pressure. Further distillation under reduced pressure gave the enamine as a colorless oil (6.47 g, 78%): ^1H NMR (CDCl_3) δ -0.02 (s, 9H ($^2J_{\text{SnH}} = 49.2$ Hz, 51.6 Hz), Me_3Sn), 1.35 (m, 1H, SnCH), 1.68 (m, 1H, ring), 1.9–2.0 (m, 3H, ring), 2.15 (m, 1H, ring), 2.28 (m, 1H, ring), 2.73 (nonet, 4H, NCH), 3.68 (t, 4H, OCH), 4.68 (m, 1H, alkenic); ^{13}C NMR (CDCl_3) δ -11.36 (SnMe_3 , $^1J_{\text{SnC}} = 307.2, 293.8$ Hz), 20.96 (C4, $^1J_{\text{SnC}} = 401.8, 384.2$ Hz), 27.28 (C5, $^2J_{\text{SnC}} = 12.5$ Hz), 27.94 (C6, $^3J_{\text{SnC}} = 53.1$ Hz), 28.65 (C3, $^2J_{\text{SnC}} = 9.2$ Hz), 48.33 (CN), 66.93 (CO), 101.62 (C2, $^3J_{\text{SnC}} = 48.3$ Hz), 145.34 (C1).

6-(Trimethylstannyl)- $\Delta^{1,9}$ -2-octalone. 1-Morpholino-4-(trimethylstannyl)cyclohexene (6.03 g, 0.018 mol) was refluxed with freshly distilled methyl vinyl ketone (1.70 mL, 0.020 mol) in 19

mL of anhydrous 1,4-dioxane for 6.5 h. Water (30 mL) was added and the mixture was refluxed for 15 h. The reaction was then diluted with 30 mL of water, saturated with NaCl, and extracted with 3×75 mL of diethyl ether. The organic layer was washed successively with 10 mL of 3 N HCl and 2×50 mL of saturated aqueous NaCl. Drying over anhydrous Na_2SO_4 and removal of solvent by rotary evaporation gave a mixture (6.65 g) that contained 37% of 2-(3-oxobutyl)-4-(trimethylstannyl)cyclohexanone and 15% of 6-(trimethylstannyl)- $\Delta^{1,9}$ -2-octalone by GC. To complete the ring closure,¹⁷ the mixture was refluxed with 0.15 mL of pyrrolidine in 9 mL of benzene for 12 h in a Dean-Stark apparatus. More pyrrolidine (0.05 mL) and benzene (8 mL) were added, and the mixture was heated for 2 days. GC analysis indicated that the last heating step did not improve the composition of products. Benzene was distilled from the reaction mixture at atmospheric pressure. The residue was distilled under reduced pressure to give a yellow oil (4.40 g, bp 120–138 °C (0.2–0.3 mmHg)), which contained 60% of 6-(trimethylstannyl)- $\Delta^{1,9}$ -2-octalone as the major component. The octalone was identified from the signals at δ 0.02 (SnMe_3) and 5.78 (alkenic) in the ^1H NMR spectra. This crude material was used directly in the next step.

***trans,cis*-6-(Trimethylstannyl)-2-decalone.** The procedure of House et al.¹⁰ was adapted for the Li-NH₃ reduction of 6-(trimethylstannyl)- $\Delta^{1,9}$ -2-octalone. The solution of crude octalone (4.39 g, 60% compound) in 16 mL of anhydrous ether with 1.45 mL of anhydrous *tert*-butyl alcohol was added to a solution of excess Li (0.40 g, 0.056 mol) in about 100 mL of liquid NH₃ at -78 °C under N₂. The mixture was stirred for 10 min and then quenched with solid NH₄Cl. After evaporation of NH₃, 60 mL of ether and 60 mL of water were added, and the layers were separated. The aqueous layer was extracted with 2×60 mL of ether. The organic layer was washed with 4×20 mL of saturated aqueous NaCl and dried over anhydrous Na_2SO_4 and MgSO_4 . Removal of solvent by rotary evaporation gave a yellow-brown oil (3.37 g), which contained 45% of 6-(trimethylstannyl)-*trans*-2-decalone as the major component. A different sample of crude octalone (3.39 g, 41% compound) prepared from 0.0183 mol of enamine was reduced similarly with a stirring time of 15 min before quenching to obtain a crude product (3.08 g) that contained 41% of the decalone. The crude product also contained unreacted octalone and the decalols from reduction of the decalone. Flash column chromatography of 2.00 g of the crude decalone in 200 g of alumina with 1/1 hexane- CHCl_3 gave an enriched sample (0.82 g, 80% by GC). Fractions were monitored by TLC on silica gel and analyzed by ^1H NMR. The final step of purification was recrystallization from pentane. The crude decalone (2.54 g) from several chromatographic separations was dissolved in about 8 mL of pentane at room temperature. The solution was cooled successively at -25, -45, and -75 °C. After the mother liquor was decanted, the solids were rinsed several times with cold pentane and then dried with a stream of N₂. Pure *trans,cis*-6-(trimethylstannyl)-2-decalone was obtained as a white powder (1.03 g, 9% overall from the enamine): ^1H NMR (CDCl_3) δ -0.01 (s, 9H ($^2J = 51.2, 49.6$ Hz), Me_3Sn), 1.0–1.4 (m, 7H, SnCH and ring), 1.65–1.72 (dq, 1H, ring), 1.8–1.95 (m, 3H, ring), 2.05 (m, 1H, ring), 2.23–2.40 (m, 3H, ring); ^{13}C NMR (CDCl_3) δ -11.93 (Me_3Sn), $^1J_{\text{SnC}} = 309.6, 295.7$ Hz), 24.17 (C6, $^1J = 397, 379.5$ Hz), 29.95 (C7, $^2J = 12.9$ Hz), 33.48 (C4), 36.38 (C8, $^3J = 67.1$ Hz), 37.00 (C5, $^2J = 12.8$ Hz), 41.70 (C3), 43.44 (C9), 43.88 (C10, $^3J = 64.1$ Hz), 48.79 (C1), 211.66 (C2); ^{119}Sn NMR (CDCl_3) δ 0.16.

***cis,trans,cis*-6-(Trimethylstannyl)-2-decalol (5-OH).** *trans,cis*-6-(Trimethylstannyl)-2-decalone (1.03 g, 3.27 mmol) in 6 mL of anhydrous diethyl ether was added to a slurry of LiAlH₄ (0.07 g, 2 mmol) in 4 mL of ether in an ice bath under N₂ and was stirred for 1 h. The reaction was quenched with 5 mL of H₂O and was treated with aqueous HCl until the precipitates disappeared. Ether (5 mL) was added, and the layers were separated. The aqueous layer was extracted with 2×15 mL of ether. The organic layers were combined and dried over anhydrous Na_2SO_4 . Removal of solvent by rotary evaporation gave a white powder (1.00 g, 96%), which by ^1H NMR was a

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mixture of 87% equatorial and 13% axial alcohols. The isomeric alcohols were separated by flash column chromatography on 200 g of alumina with a mixture of 70% hexane and 30% ethyl acetate as eluant. Fractions were monitored by TLC on silica gel and analyzed by ^1H NMR. The axial alcohol eluted first and was obtained as a white powder (0.10 g, 10%). Pure equatorial alcohol was recovered from the later fractions as fine, white needles (0.64 g, 62%): ^1H NMR (CDCl_3) δ -0.033 (s, 9H ($^2J = 51.6, 49.2$ Hz), Me_3Sn), 0.8–1.35 (m, 9H, SnCH and ring), 1.41 (d, 1H, OH), 1.55–2.0 (m, 6H, ring), 3.57 (t of q, 1H, CHO); ^{13}C NMR (CDCl_3) δ -11.97 (Me_3Sn , $^1J_{\text{SnC}} = 306.0, 292.0$ Hz), 24.72 (C6, $^1J = 403, 385$ Hz), 30.60 (C7, $^2J = 13.8$ Hz), 31.72 (C4), 35.82 (C3), 35.92 (C8, $^3J = 67.8$ Hz), 37.51 (C5, $^2J = 14.3$ Hz), 41.24 (C9), 43.36 (C1), 44.49 (C10, $^3J = 64.7$ Hz), 70.72 (C2); ^{119}Sn NMR (CDCl_3) δ -1.35; MS m/z 318 (M^+ , 32%), 303 (20), 165 (100), 151 (27), 135 (24), 93 (19), 79 (18), 67 (31), 41 (24). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: C, 49.25; H, 8.27; Sn, 37.44. Found: C, 49.30; H, 8.36; Sn, 37.13.

trans,trans,cis-6-(Trimethylstannyl)-2-decalol (6-OH). *trans,cis-6*-(Trimethylstannyl)-2-decalone (1.55 g, 4.90 mmol) in 6 mL of anhydrous THF was added dropwise to a solution of potassium *tri-sec*-butylborohydride (5.20 mL, 1.0 M in THF, Aldrich) and the mixture was stirred for 3 h at -78°C . The reaction was quenched with 5 mL of H_2O , 5 mL of 2 N NaOH, and 5 mL of 30% H_2O_2 at 0°C . After stirring for 3 h at room temperature, the mixture was extracted with 4×30 mL of hexane. The organic layer was washed with 2×30 mL of saturated aqueous NaCl. Removal of solvent under reduced pressure gave 1.53 g (98%) of a white powder, which by ^1H NMR was a 92/8 mixture of axial/equatorial alcohols. Recrystallization from pentane of 0.50 g of material gave 0.39 g (76% overall) of pure axial alcohol: ^1H NMR (CDCl_3) δ -0.037 (s, 9H ($^2J = 51.6, 49.2$ Hz), Me_3Sn), 0.85–1.85 (m, 16H, ring and OH), 4.07 (m, 1H, CHO); ^{13}C NMR (CDCl_3) δ -12.00 (Me_3Sn , $^1J_{\text{SnC}} = 305.0, 291.3$ Hz), 24.84 (C6, $^1J = 403.6, 386.0$ Hz), 27.20 (C4), 30.93 (C7, $^2J = 14.3$ Hz), 32.93 (C3), 35.94 (C8, $^3J = 67.3$ Hz), 36.52 (C9), 37.98 (C5, $^2J = 14.7$ Hz), 40.46 (C1), 45.29 (C10, $^3J = 65.2$ Hz), 66.91 (C2); ^{119}Sn NMR (CDCl_3) δ -1.91; MS m/z 318 (M^+ , 36%), 303 (28), 165 (100), 151 (26), 135 (21), 93 (14), 79 (14), 67 (23), 41 (15). Anal. Calcd for $\text{C}_{13}\text{H}_{26}\text{OSn}$: C, 49.25; H, 8.27; Sn, 37.44. Found: C, 49.29; H, 7.79; Sn, 37.10.

cis,trans,cis-6-(Trimethylstannyl)-2-decalyl Tosylate (5-OTs). The tosylate was prepared according to the standard Tipson¹² procedure. *cis,trans,cis-6*-(Trimethylstannyl)-2-decalol (5-OH, 0.31 g, 1 mmol) was reacted with tosyl chloride (0.37 g, 2 mmol) in 5.20 mL of pyridine for 2 days at about 5°C . The product was recrystallized twice from hexane to give white crystals (0.40 g, 87%, mp 76 – 77°C): ^1H NMR (CDCl_3) δ -0.05 (s, 9H ($^2J = 51.2, 49.2$ Hz) Me_3Sn), 0.76–1.96 (m, 15H, ring), 2.42 (s, 3H, ArCH_3), 4.38 (m, 1H, CHO), 7.29 (d, 2H, Ar), 7.76 (d, 2H, Ar); ^{13}C NMR (CDCl_3) δ -12.00 (Me_3Sn , $^1J_{\text{SnC}} = 307.6, 293.8$ Hz), 21.60 (ArCH_3), 24.38 (C6, $^1J = 398.6, 381.6$ Hz), 30.31 (C7, $^2J = 13.8$ Hz), 31.36 (C4), 32.73 (C3), 35.53 (C8, $^3J = 67.2$ Hz), 37.14 (C5, $^2J = 13.9$ Hz), 39.92 (C1), 41.14 (C9), 43.84 (C10, $^3J = 65.5$ Hz), 81.90 (C2), 127.55, 129.68, 137.74, 144.27 (aromatic); ^{119}Sn NMR (CDCl_3) δ -0.67.

trans,trans,cis-6-(Trimethylstannyl)-2-decalyl tosylate (6-OTs) was prepared by the Tipson procedure¹² from *trans,trans,cis-6*-(trimethylstannyl)-2-decalol (6-OH, 0.06 g, 0.2 mmol) to produce fine, white needles of pure axial tosylate (0.048 g, mp 83 – 84°C): ^1H NMR (CDCl_3) δ -0.04 (s, 9H ($^2J = 51.2, 49.3$ Hz), Me_3Sn), 0.78–1.85 (m, 15H, ring), 2.41 (s, 3H, ArCH_3), 4.76 (m, 1H, CHO), 7.30 (d, 2H, Ar), 7.77 (d, 2H, Ar); ^{13}C NMR (CDCl_3) δ -12.01 (Me_3Sn , $^1J_{\text{SnC}} = 306.6, 293.1$ Hz), 21.59 (ArCH_3), 24.59 (C6), 27.09 (C4), 30.63 (C7, $^2J = 14.1$ Hz), 30.79 (C3), 35.47 (C8, $^3J = 67.4$ Hz), 36.46 (C9), 37.60 (C5, $^2J = 14.6$ Hz), 38.08 (C1), 44.56 (C10, $^3J = 65.1$ Hz), 80.17 (C2), 127.59, 129.67, 134.65, 144.25 (aromatic); ^{119}Sn NMR (CDCl_3) δ -1.28.

trans-2-Decalols (7-OH and 8-OH). The mixture of isomeric alcohols (1.38 g, Aldrich Rare Chemicals) was separated by flash column chromatography on alumina (225 g) with a mixture of 70% hexane and 30% ethyl acetate as the solvent system. *trans,trans-2*-Decalol (8-OH, 0.38 g, 28%) was recovered as a white solid from the early fractions. A mixture of mostly *cis,trans-*

2-decalol (7-OH) from the later fractions was recrystallized twice from hexane to obtain white crystals of the equatorial alcohol (0.32 g, 23%). Characterization of *cis,trans-2*-decalol: ^1H NMR (CDCl_3) δ 0.75–2.0 (m, 17H, ring and OH), 3.56 (m, 1H, CHO); ^{13}C NMR (CDCl_3) δ 26.26, 26.51, 31.96 (C4), 33.23, 33.76, 35.78 (C3), 41.15 (C9), 42.27 (C10), 43.20 (C1), 70.78 (C2); MS m/z 154 (M^+ , 1%), 136 (100), 121 (30), 107 (21), 95 (44), 81 (20), 67 (26), 55 (26), 41 (24). Characterization of *trans,trans-2*-decalol: ^1H NMR (CDCl_3) δ 0.8–1.8 (m, 17H, ring and OH), 4.07 (m, 1H, CHO); ^{13}C NMR (CDCl_3) δ 26.59 (C6, C7) 27.48 (C4), 32.87 (C8), 33.72 (C3 or C5), 33.81 (C3 or C5), 36.42 (C9), 40.31 (C1), 43.06 (C10), 66.96 (C2); MS m/z 154 (M^+ , 3%), 136 (100), 121 (29), 107 (24), 95 (40), 81 (28), 67 (34), 55 (33), 41 (31). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: C, 77.87; H, 11.76. Found: C, 77.96; H, 11.80.

trans-2-Decalyl Tosylates (7-OTs and 8-OTs). The decalols were converted to their respective tosylates in the usual manner.¹² The yields were 62% for *cis,trans-2*-decalyl tosylate (7-OTs, 0.21 g, mp 65 – 66°C (lit.¹⁸ 65°C)) and 56% for *trans,trans-2*-decalyl tosylate (8-OTs, 0.19 g, mp 104°C (lit.¹⁸ 111°C)). Characterization of *cis,trans*-decalyl tosylate: ^1H NMR (CDCl_3) δ 0.75–1.95 (m, 16H, ring), 2.42 (s, 3H, ArCH_3), 4.39 (m, 1H, CHO), 7.30 (d, 2H, Ar), 7.76 (d, 2H, Ar); ^{13}C NMR (CDCl_3) δ 21.62 (ArCH_3), 25.99, 26.26, 31.61, 32.71, 32.86, 33.41, 39.80, 41.06 (C9 or C10), 41.65 (C9 or C10), 82.02 (C2), 127.57, 129.70, 134.73, 144.29 (aromatic). Characterization of *trans,trans-2*-decalyl tosylate: ^1H NMR (CDCl_3) δ 0.85–1.85 (m, 16H, ring), 2.42 (s, 3H, ArCH_3), 4.77 (m, 1H, CHO), 7.30 (d, 2H, Ar), 7.77 (d, 2H, Ar); ^{13}C NMR (CDCl_3) δ 21.61 (ArCH_3), 26.33, 26.42, 27.39, 30.77, 33.38, 36.37, 37.96, 42.28, 80.26 (C2), 127.61, 129.68, 134.66, 144.26 (aromatic).

Kinetic Rates. Solvents were prepared according to published procedures.¹⁹ Rates of solvolyses were determined by conductance measurements on 25 mL of approximately 10^{-3} M solutions in a conductance cell with Pt electrodes and a capacity of 35 mL. The cell was either heated with a Precision H8 bath or cooled with a Techne RB-5 bath to constant temperature. Temperatures at 50°C or lower were measured with a factory-certified (NBS) thermometer (0.1 $^\circ\text{C}$ division, -1 – 51°C). Other temperatures were measured with a Thermoschneider thermometer (0.2 $^\circ\text{C}$ division, 40 – 100°C), which had been calibrated against an NBS-certified thermometer. The change in conductance was followed with a YSI model 32 conductance meter. The rate constant, k , was calculated by LOTUS 1-2-3 regression analysis from the linear equation $\ln(n_{\infty} - n_t) = \text{constant} - kt$, in which n_{∞} is the infinity conductance and n_t is the conductance at time t , using data points collected for 1–3 half-lives.

Product Studies. The products of solvolysis in perdeuterated 80% ethanol were determined from ^1H , ^{13}C , and ^{119}Sn NMR analysis of about 0.2 M solutions of the ester in sealed NMR tubes after greater than 10 half-lives. Except for reactions done at room temperature, the sealed tubes were immersed in a water bath at 50 or 75°C . Progress of the reaction was monitored by ^1H NMR. Product yields were calculated from the integration of proton resonances.

Crystal Structure Analysis. A colorless crystal of *cis,trans,cis-6*-(trimethylstannyl)-2-decalyl tosylate (5-OTs) was obtained by slow cooling of a methanol solution. The transparent, prismatic crystal with approximate dimensions of $0.43 \times 0.34 \times 0.11$ mm was mounted on a glass fiber with grease. Data were collected at $-120 \pm 1^\circ\text{C}$ on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 centered reflections in the range $19.90^\circ < 2\theta < 23.80^\circ$. The compound has a formula weight of 471.22 and belongs to the monoclinic space group $P2_1/n$ (no. 14) with $a = 6.802(4)$ Å, $b = 26.723(6)$ Å, $c = 12.278(2)$ Å, $\beta = 104.68(2)^\circ$, $V = 2159(2)$ Å³, $Z = 4$, and a calculated density of 1.450 g/cm³. Diffraction intensities were collected using the ω - θ scan technique to a maximum 2θ of 54.0° . Of the

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5227 reflections that were collected, 4830 were unique ($R_{\text{int}} = 0.073$). The linear absorption coefficient for Mo $K\alpha$ is 12.9 cm^{-1} . An analytical absorption correction was applied that resulted in transmission factors of 0.63–0.86. Lorentz and polarization corrections were applied. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were independently refined with isotropic thermal parameters. The final cycle of full-matrix least-squares refinement was based on 3274 reflections ($I > 3.00\sigma(I)$) and 354 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.045$ and $R_w = 0.054$. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.57 and $-0.97 \text{ e}/\text{\AA}^3$, respectively. The highest peak in the final difference map was located in the vicinity of tin. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp. Addi-

tional crystallographic details are presented in the supplementary material.²⁰

Supplementary Material Available: Description of the X-ray structure of 5-OTs, including experimental procedures, positional and thermal parameters, temperature factors, bond distances, bond angles, torsional angles, intramolecular contacts, and ORTEP representations (31 pages). This material is contained in libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(20) The author has deposited atomic coordinates for 5-OTs 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.