

Effects of Bridgehead Metalloidal Substituents (MMe₃, M = Si and Sn) on the Stability of the 1-Norbornyl Cation

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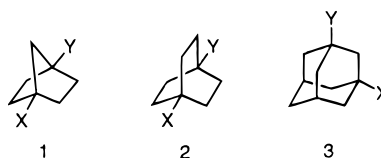
Received June 3, 1996[⊗]

Abstract: 4-Metalloidal (MMe₃, M = Si and Sn)-substituted bicyclo[2.2.1]hept-1-yl triflates (**1**, Y = OSO₂CF₃) have been synthesized and their solvolyses in aqueous ethanol and trifluoroethanol have been examined together with those of the parent and methyl derivatives (**1**, Y = OSO₂CF₃; X = H and Me, respectively). Large rate enhancement factors are observed for the metalloidal substituents. A comparison of these accelerative effects with the corresponding values in the bicyclo[2.2.2]octane and adamantane ring systems (**2**, Y = OSO₂Me, and **3**, Y = Br, respectively) indicates the substrate order of these effects is **1** > **2** >> **3**. Qualitative considerations lead to the pronounced effects in **1** being ascribed to “back-lobe” through-space effects (homohyperconjugation). A more quantitative picture of the stabilizing effects of SiMe₃ and SnMe₃ on the 1-norbornyl cation (**5**) is painted by high-level *ab initio* (MP2/6-31G(d)[DZP]) molecular orbital calculations. The calculations provide strong support for the homohyperconjugative stabilizing effects of these groups but indicate that the weak accelerative effect of 4-methyl in **1** (Y = OSO₂CF₃, X = Me) is more likely a manifestation of dominant destabilizing ground-state effects. Furthermore, the high-level calculations expose that the usual practice of theoretical modeling of SiMe₃ by use of SiH₃ to reduce the complexity of the computational problem can be seriously inadequate.

Introduction

The rigid molecular framework of polycyclic alkanes makes these systems attractive model substrates for the delineation of substituent electronic effects in the absence of complicating conformational and proximity phenomena. In particular, their use in defining the effects of metalloidal substituents on the rates of cation mediated reactions has significantly illuminated the concepts of long-range (beyond two bonds) electron delocalization phenomena in saturated systems. To date these studies have embraced several polycyclic ring systems (adamantane,^{1,2} bicyclo[2.2.2]octane,³ cubane,⁴ and norbornane⁵) and significant γ - and δ -donor effects have been uncovered which have their origin in through-space (TS) and through-bond (TB) interactions.

Herein we report an extension of our previous endeavors in the bicyclo[2.2.2]octane and adamantane ring systems with metalloidal groups (SiMe₃ and SnMe₃)^{2,3} to the 1,4-disubstitution of the norbornane ring system (**1**). This system is of interest because the intervening connective bonds between the bridgehead positions provide a different blend of possible TS and TB interactions compared to 1,4-disubstituted bicyclo[2.2.2]octanes (**2**) and 1,3-disubstituted adamantanes (**3**). The major impetus behind this study was the recent attention drawn by Lambert et



al.⁶ to the surprisingly weak stabilizing γ effects of the SiMe₃ and SnMe₃ groups in the adamant-1-yl cation (**4**), as revealed by small accelerative solvolytic rate factors for **3** (Y = Br; 8.6^{1b,c} and 58^{1a} for SiMe₃ and SnMe₃ in 80 vol % aqueous ethanol (80E), respectively). These γ effects in the adamantane ring system appear considerably weaker than those observed in the more flexible cyclohexyl framework.^{6,7} This led Lambert et al.⁶ to speculate that the TS interaction between the C–M (M = Si or Sn) bond and the empty carbocation orbital (homohyperconjugative γ effect) may be weak in the comparatively rigid polycyclic system due to the long 1,3-distance between the bridgehead carbons precluding optimization of the interaction. Thus, since the comparable internuclear distance in the norborn-1-yl cation (**5**) is expected to be substantially shorter than that in **4** (1.99 Å⁸ vs 2.34 Å⁹, respectively), we felt that an examination of metalloidal substituent effects on the stability of **5** might provide insight into how finely tuned TS interactions are with respect to the following factors: (i) internuclear distance; (ii) flexibility of the substrate; and (iii) electron demand.

Consequently, we have prepared appropriate derivatives of **1** (X = SiMe₃ and SnMe₃; Y = OSO₂CF₃) and measured their rates of solvolysis in aqueous ethanol and trifluoroethanol

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

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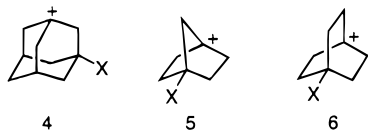
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solvents. In this paper we report the results of this work together with high-level *ab initio* calculations of systems **1** (Y = H) and **5** where X = H, CH₃, SiH₃, SiMe₃, and SnMe₃.

Results and Discussion

The rate constants for the solvolysis of the 4-substituted (MMe₃; M = Si and Sn) bicyclo[2.2.1]hept-1-yl triflate esters (**1**, Y = OSO₂CF₃) are listed in Table 1 together with those of the parent compound (X = H)¹⁰ and the corresponding methyl derivative (X = CH₃).¹¹ Except for the latter compound, rate constants are reported at 25 °C for both solvents (80 vol % ethanol with 20 vol % water (80E) and 97 wt % trifluoroethanol–3 wt % water (97T)). However, the parent and silicon compounds (X = H and SiMe₃) react too slowly at this temperature to be conveniently measured directly by the NMR technique employed (see Experimental Section). Consequently, the solvolysis rate constants for these compounds were determined at higher temperatures¹⁰ and the 25 °C values were obtained by extrapolation with the appropriate Arrhenius equations 1–4. The precision of fit for each equation is

$$\ln k = (-1.404 \times 10^4)(1/T) + 27.068 \quad (1)$$

$$(X = \text{H}, 80\text{E})$$

$$\ln k = (-1.348 \times 10^4)(1/T) + 26.653 \quad (2)$$

$$(X = \text{H}, 97\text{T})$$

$$\ln k = (-1.408 \times 10^4)(1/T) + 31.477 \quad (3)$$

$$(X = \text{SiMe}_3, 80\text{E})$$

$$\ln k = (-1.056 \times 10^4)(1/T) + 24.053 \quad (4)$$

$$(X = \text{SiMe}_3, 97\text{T})$$

significantly better than $r = 0.99$. It should be noted at this point that a comparison of eqs 1 and 3 reveals that the activation energies (E_a) for the parent and silicon compounds (X = H and SiMe₃) in 80E (27.90 and 27.93 kcal/mol, respectively) are practically identical! This is clearly not the situation in 97T (cf. eqs 2 and 4; 26.77 and 20.98 kcal/mol, respectively). We shall return to this intriguing result later on in the discussion.

It can be seen (Table 1) that the solvolysis rates of the parent norbornyl system (X = H) are extremely slow for both solvent systems even with the very powerful triflate leaving group. Its half-life in 80E at 25 °C is ca. 11 years and it is at least 10⁶ times less reactive than the corresponding bicyclo[2.2.2]octyl triflate (**2**, Y = OSO₂CF₃; X = H).¹² In fact it has been shown to be less reactive than even cubyl triflate.¹³ This unreactivity of bicyclo[2.2.1]hept-1-yl derivatives toward S_N1 solvolysis has

(10) (a) We are grateful to Dr. E. W. Della for supplying us with a sample of 1-norbornyl triflate and, as well, providing us with rate data for this compound at higher temperatures prior to publication.^{10b} (b) Della, E. W.; Janowski, W. K. *J. Org. Chem.* **1995**, *60*, 7756 and references cited therein.

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Table 1. Solvolysis Rate Constants^a for 4-Substituted (X) Bicyclo[2.2.1]hept-1-yl Triflates (**1**, Y = OSO₂CF₃)

X	solvent ^b	T (°C)	k (s ⁻¹)
H	80E	25.0	1.96 × 10 ⁻⁹ ^{c,d}
H	80E	80.0	2.99 × 10 ⁻⁶
H	60E	80.3	1.08 × 10 ⁻⁵ ^e
CH ₃	80E	80.0	1.17 × 10 ⁻⁵ ^f
CH ₃	60E	80.3	4.04 × 10 ⁻⁵ ^e
SiMe ₃	80E	25.0	1.53 × 10 ⁻⁷ ^c
SiMe ₃	80E	40.0	1.47 × 10 ⁻⁶
SiMe ₃	80E	50.0	5.87 × 10 ⁻⁶
SiMe ₃	80E	60.0	2.19 × 10 ⁻⁵
SnMe ₃	80E	25.0	6.98 × 10 ⁻⁶
H	97T	25.0	8.64 × 10 ⁻⁹ ^c
H	97T	70.0	3.37 × 10 ⁻⁶
H	97T	79.9	9.26 × 10 ⁻⁶
H	97T	89.8	2.87 × 10 ⁻⁵
H	97T	60.2	1.03 × 10 ⁻⁶ ^c
CH ₃	97T	60.2	7.63 × 10 ⁻⁶ ^f
SiMe ₃	97T	25.0	1.14 × 10 ⁻⁵ ^c
SiMe ₃	97T	55.0	2.90 × 10 ⁻⁴
SiMe ₃	97T	60.0	4.89 × 10 ⁻⁴
SiMe ₃	97T	65.0	7.13 × 10 ⁻⁴
SiMe ₃	97T	70.0	1.23 × 10 ⁻³
SnMe ₃	97T	25.0	1.77 × 10 ⁻⁴

^a First-order rate constants (experimental error ±5%). ^b 60E and 80E are 60 and 80 vol % ethanol with 40 and 20 vol % water while 97T is 97 wt % trifluoroethanol–3 wt % water. ^c Extrapolated from rates observed at higher temperatures. ^d See ref 10. ^e Taken from ref 11b. ^f See ref 23b.

Table 2. Relative Solvolysis Rates for 4-Substituted (X) Bicyclo[2.2.1]hept-1-yl Triflates (**1**, Y = OSO₂CF₃)

solvent	CH ₃ /H	Me ₃ Si/H	Me ₃ Sn/H	Me ₃ Sn/Me ₃ Si
60E	3.74 ^a			
80E	3.91 ^b	78.1 ^d	3,561.2 ^d	45.6 ^d
97T	7.41 ^c	1,319.4 ^d	20,486.1 ^d	15.5 ^d

^a 80.3 °C. ^b 80.0 °C. ^c 60.2 °C. ^d 25.0 °C.

long been known¹⁴ and is attributed largely to an increase in strain energy on forming the bridgehead cation species,^{10b,15} i.e. the molecular skeleton precludes the attainment of the preferred planar geometry for a carbocation. However, it can be seen (Table 1) that the introduction of metalloidal substituents (SiMe₃ and SnMe₃) at the 4-position leads to marked rate accelerations which are much larger than those observed for Me. This is more clearly revealed from the relative rates listed in Table 2. In accord with expectations from other studies^{2,3} the enhanced reactivities are more pronounced in 97T than 80E because charge dispersal within the cation of the transition state is larger in the former than the latter medium. Hence more demand is placed on the conjugative abilities of the C–M bonds. Before analyzing these rate enhancement factors further, it is instructive to note that similar to the product distributions previously reported for the parent¹⁶ and methyl compounds,^{11b} and confirmed here (Table 3), only direct substitution products were identified for the SiMe₃ and SnMe₃ derivatives of **1** (Y = OSO₂CF₃; Table 3). This is in accord with expectations for a unimolecular ionization reaction, thus establishing strongly the intermediacy of the respective 1-norbornyl cations (**5**, X = SiMe₃ and SnMe₃). Interestingly, there was no evidence of desilylation or destannylation products as might have been the case if [2.2.1]propellane was formed as an intermediate either concertedly or after the ionization process. This highly reactive species^{17,18} would have been trapped readily by the solvent to

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Table 3. Product Distribution Analysis of the Solvolysis of **1** (Y = OSO₂CF₃)

X	solvent	product distribution (%) ^a	
		alcohol	ether
H	80E	53	47
CH ₃	80E	54	46
SiMe ₃	80E	61	39
SnMe ₃	80E	53	47
H	97T	14	86
CH ₃	97T	15	85
SiMe ₃	97T	18	82
SnMe ₃	97T	23	77

^a Determined by VPC.

form the desilylated or destannylated products. The product analysis also revealed that no Grob fragmentation¹⁹ product (1,3-dimethylenecyclopentane) was formed from the respective cations.

Insight into the origin of the dramatic rate enhancement factors for SiMe₃ and SnMe₃ in system **1** (Y = OSO₂CF₃; Table 2) is achieved by comparisons with the corresponding values for systems **2** (Y = OSO₂Me; Me₃Si/H = 18.6 (80E), 48.6 (97T); Me₃Sn/H = 781 (80E), 2841 (97T))³ and **3** (Y = Br; see Introduction). Clearly the substrate order of these effects is **1** > **2** >> **3**. The accelerative effects for the latter two systems have been ascribed to stabilizing TB (double hyperconjugation)^{3,20} and TS (homohyperconjugation or back-lobe interactions)¹ effects, respectively, of the cationic transition states which resemble **4** and **6**. Both these electron delocalization mechanisms are capable of contributing to the stabilization of the cationic transition state (resembles **5**) for the solvolysis of **1** (Y = OSO₂CF₃) (denoted by canonical structures **7** and **8**, respectively). Homohyperconjugation is dependent on the extent



of overlap of the back-lobe orbitals and, hence, on their relative orientation (interorbital angle and internuclear distance between the bridgehead positions).^{9,21,22} On the other hand, the extent of double hyperconjugation is determined by the number of bridging ethano bonds as well as their geometric alignment (the effect is optimized when the participant orbitals have an antiperiplanar relationship).^{2,21} With respect to the enhanced reactivities of SiMe₃ and SnMe₃ in **1**, a consideration of these factors governing the efficacy of transmission of the two electronic mechanisms clearly points to homohyperconjugation as the mechanism most likely to be largely responsible. However, some stabilizing "leakage" from double hyperconjugation through the unfavorably aligned orbitals in **5** cannot be discounted by these qualitative considerations.

The weak accelerative effect for Me in **1** (Y = OSO₂CF₃; Table 2), previously noted by Martinez et al.,^{11b,23} is of particular interest because it stands in stark contrast to the feeble decelerating effects of this group in **2** and **3** (**2**, Y = *p*-NO₂C₆H₄-

SO₂O, Me/H = 0.25 (80E);²⁴ **3**, Y = Br, Me/H = 0.74 (80E);^{1a} **3**, Y = *p*-CH₃C₆H₄SO₂O, Me/H = 0.78 (80E)).²⁵ The results for the latter two systems are in line with a large body of NMR and reactivity data from polycycloalkane model system^{13,26–29} studies on γ - and δ -effects which suggests that Me is a weak σ -electron withdrawing group. It is not clear from qualitative considerations whether the π -donor capacity of the Me group can provide an explanation for the accelerative result for **1** (Y = OSO₂CF₃) since it is not obvious that the requisite symmetry and spatial requirements are met by the LUMO orbital.¹⁵

In order to illuminate further the aforementioned stabilizing effects of CH₃, SiMe₃, and SnMe₃ on the 1-norbornyl cation (**5**, X = H, CH₃, SiMe₃, and SnMe₃), we sought recourse to high-level *ab initio* (MP2/6-31G(d)[DZP]) molecular orbital calculations. Borden¹⁵ and we⁸ have shown that the relative rates of solvolysis of a variety of highly-strained bridgehead systems are accurately predicted by calculating the relative energy differences between the corresponding cation (R⁺) and parent structure (RH). The inclusion of polarization functions and electron correlation (MP2) was essential in order to reproduce the experimentally-observed trends.

Other workers^{20,22,30} have calculated the effect of the silyl (SiH₃) substituent as a model for the trimethylsilyl group. In this work, we include this substituent for comparison. In our systems SiH₃ proved not to model SiMe₃ well (see later); MP2/6-31G(d)[DZP] calculations predict significant differences in structure and relative energy of cations **5** (X = SiH₃, SiMe₃).

Calculations were performed using the Gaussian 92 or Gaussian 94 system of programs^{31,32} on a Sun SparcServer 10/512 or Cray Y-MP4E/364 computer. The 6-31G* basis was used for H, C, and Si, while the (valence) double- ζ pseudo-potential basis of Hay and Wadt³³ supplemented with a single set of d-functions (exponent $d(\zeta)$) as recommended by Höllwarth and co-workers³⁴) was used on Sn. This basis set is referred to as 6-31G(d)[DZP] throughout this work. Structures in this study were fully optimized at the MP2/6-31G(d)[DZP] level of theory

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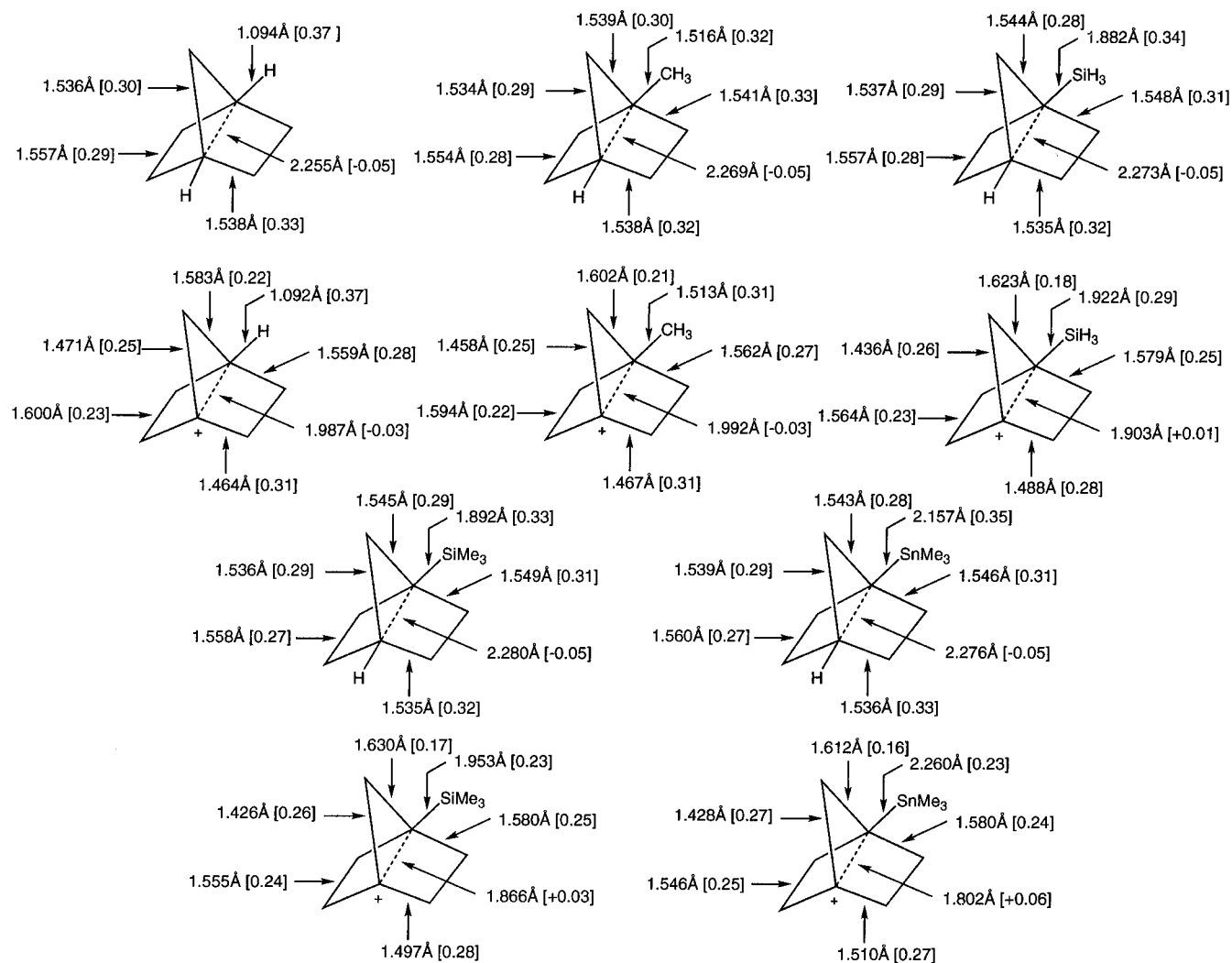


Figure 1. Selected MP2/6-31G(d)[DZP]-calculated distances and bond populations [square brackets].

using standard gradient-optimization techniques.³⁵ Mulliken population analyses were performed on the MP2/6-31G(d)-[DZP]-calculated wave function in each case. Important features are displayed in Figure 1.

The calculated differences in energy between the cation and parent structure (**1** → **5**) in each case relative to the same difference for the norbornyl cation (**1**, Y = H → **5**, Y = H) are listed in Table 4 together with the MP2/6-31G(d)[DZP]-calculated energies of the structures in question. Inspection of Table 4 reveals clearly the effect of the various substituents on the relative stability of the cations (**5**). All substituents have the effect of reducing the energy required in the formation of the cation relative to the parent norbornyl system. It is interesting to note the predicted effects of the silyl (SiH₃) and trimethylsilyl (Me₃Si) groups. The former substituent stabilizes the cation by some 3 kcal·mol⁻¹, less than the stabilization afforded by the methyl group, while the latter is predicted to lower the relative energy of the cation by a dramatic 11.1 kcal·mol⁻¹ over the norbornyl system.

When the MP2/6-31G(d)[DZP]-calculated relative energy for the formation of the cation (**5**) (Table 4) is plotted against log *k*_{rel} (Table 2), a pleasing correlation is observed (Figure 2). This correlation provides strong evidence that the calculations

Table 4. MP2/6-31G(d)[DZP]-Calculated Energies of the Cations (**5**) and Parent Structures (**1**) in This Study

structure	<i>E</i> ^a	<i>E</i> (5) - <i>E</i> (1) ^b
5 (X = H)	-272.065 93	0
1 (X = H)	-272.975 91	
5 (X = SiH ₃)	-562.227 45	-3.0
1 (X = SiH ₃)	-563.132 67	
5 (X = Me)	-311.243 70	-3.5
1 (X = Me)	-312.148 13	
5 (X = SiMe ₃)	-679.779 66	-11.1
1 (X = SiMe ₃)	-680.671 92	
5 (X = SnMe ₃)	-394.052 97	-15.5
1 (X = SnMe ₃)	-394.938 23	

^a Energies in hartrees (1 hartree = 627.5 kcal·mol⁻¹). ^b Energies in kcal·mol⁻¹ relative to *E*(**5**, X = H) - *E*(**1**, X = H), i.e. relative hydride affinities with respect to the parent ion.

presented in this work provided an accurate ordering of the relative energies of 4-substituted 1-norbornyl cations. It should be noted that the relative data for 97T were chosen for the correlation rather than that for 80E because charge dispersal within the cation of the transition state is larger in the former weakly nucleophilic medium.³ Hence, these data best approximate the intrinsic electronic effects of the groups in the gas phase as determined by the calculations.

Figure 1 reveals the important role that the substituent (X) plays in stabilizing the cations (**5**). Both the bond length and (Mulliken) bond population data suggest that resonance struc-

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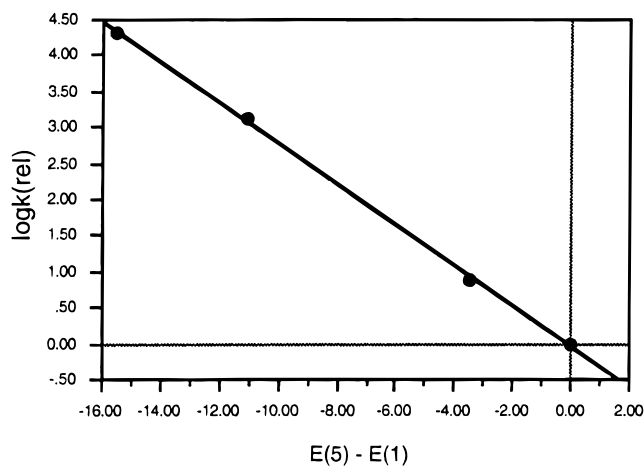
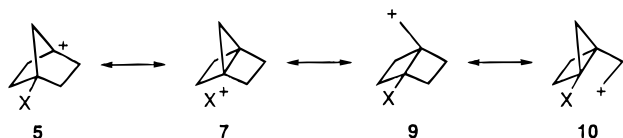
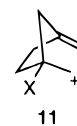


Figure 2. Plot of logarithms of the relative solvolysis rates (97T) for **1**, $Y = \text{OSO}_2\text{CF}_3$ ($\log k(\text{rel})$) vs $E(5) - E(1)$ ($\text{kcal}\cdot\text{mol}^{-1}$) ($y = -0.282x - 0.045$, $r^2 = 0.999$).

tures (**7**, **9**–**10**) are important contributors to the overall structure



of **5** when silicon and tin substituents are present. Significantly, the shortening of the C(1)–C(4) separation from 1.987 Å in the parent cation (**5**, X = H) to 1.903 Å (SiH₃), 1.866 Å (SiMe₃), and 1.802 Å (SnMe₃) together with a lengthening of the C(4)–X bond when compared with **1** (1.922 Å vs 1.882 Å, X = SiH₃; 1.953 Å vs 1.892 Å, X = SiMe₃; 2.260 Å vs 2.157 Å, X = SnMe₃) are indicative of substantial involvement of resonance contributor (**7**), a result of the interaction of the back-lobe of the C–X bond with the vacant (cationic) p-orbital in **5**. This is further supported by the observed change in C(1)–C(4) bond populations. All of the neutral species (**1**) are predicted to have antibonding interactions between bridgeheads, with calculated populations of –0.05 in each case. This interaction in the parent cation is also predicted to be antibonding in nature, with a calculated population of –0.03. This antibonding character is essentially neutralized when the silyl (SiH₃) substituent is introduced (+0.01) and becomes bonding in nature with trimethylsilyl and trimethylstannyl substitution, with calculated C(1)–C(4) bond populations of +0.03 and +0.06, respectively. Structure **7** would be expected to be increasingly more important with the decrease in electronegativity in progressing from silicon to tin (SiH₃ > SiMe₃ > SnMe₃). It is important to note that in the absence of a significant stabilizing homohyperconjugative mechanism the SiH₃ substituent would act to destabilize **5** as a result of having a significant electron-withdrawing electrostatic field influence ($\sigma_F = 0.16$).^{36a,b} In this respect it differs markedly from SiMe₃ and SnMe₃ which both have σ_F values close to zero.³⁶ Thus, it is not surprising that high-level calculations reveal a much smaller stabilizing effect on **5** by SiH₃ than SiMe₃. The result clearly highlights that theoretical modeling of SiMe₃ by use of SiH₃ in order to simplify the computational problem can be an inappropriate expedient. The data presented in Figure 1 also support the involvement to a lesser extent of contributors **9** and **10** to the overall structure of the cation but not **8** and **11** which denote double hyperconjugation and hyperconjugation, respectively. In comparing the



cations (**5**) with the parent structures (**1**) a significant weakening of the of the C(3)–C(4) and C(4)–C(7) bonds is observed. Rehybridization at C(1) makes it difficult to compare C(1)–C(2) and C(1)–C(7) separations and populations.

It is clear that contributor **7** is unimportant when the substituent (X) is methyl or hydrogen; both C(4)–CH₃ and C(4)–H bonds exhibit little change in length and bond population between cation (**5**) and parent (**1**). In addition, both cations (**5**, X = H, CH₃) exhibit similar C(1)–C(4) antibonding interactions (–0.03). It would appear that the back-lobe of a C–H or C–C bond provides insufficient overlap with the vacant p-orbital in the cations (**5**, X = H, CH₃) to become an important stabilizing feature. The shorter C(1)–C(2) and longer C(2)–C(3) distances when X = H, CH₃ when compared with the other cations (**5**) together with associated differences in bond populations suggest that structure **11** plays a role in stabilizing norbornyl cations bearing hydrogen or methyl bridgehead substitution (**5**, X = H, CH₃).

It is also interesting to compare the (Mulliken) calculated charge distribution in the cations (**5**), particularly the total charge residing on substituent X. We have corrected for the intrinsic polarization of the C(4)–X bond by adding the calculated (negative) charge at position 4 to that calculated for group X. Values of +0.06 (H), +0.08 (CH₃), +0.10 (SiH₃), +0.20 (SiMe₃), and +0.24 (SnMe₃) are obtained in this manner. These values are consistent with our aforementioned analysis; methyl substitution at C(4) provides little stabilization to the cation (**5**), while the metalloidal substituents provide stabilization through involvement of contributor **7**.

Given the similarities between cations (**5**, X = H, CH₃) the question of why methyl substitution results in an increase in the observed rate of solvolysis relative to the norbornyl system needs to be addressed. We believe that the answer to this question may well lie in destabilization of 1-methylnorbornane (**1**, X = CH₃) (and hence the triflate) over the unsubstituted system (**1**, X = H). Inspection of the C(1)–C(4) distances in the parent compounds (**1**) shows general, albeit small, increases from a value of 2.255 Å (X = H) to 2.269 (CH₃), 2.273 (SiH₃), and 2.280 Å (SiMe₃), with a slight decrease to 2.276 Å when the trimethylstannyl group is included. These data suggest that the parent molecules (**1**) are destabilized by the introduction of group(IV) substituents at the bridgehead. Wiberg and McMurdie reported recently MP2/6-31G* calculations which predict that the bridgehead–bridgehead separations in 1-substituted bicyclo[1.1.1]pentanes are dependent on both the electronegativity of the substituent and the size of the back-lobe of the bridgehead C–X bond.²⁹ Second-row elements give rise to greater 1,3-separations than first-row elements of similar electronegativity.

It would appear, therefore, that the calculated energy differences ($E(5) - E(1)$) and associated rates of solvolysis are dependent on a delicate balance of cation stabilization through canonical structure (**7**) and parent destabilization through bridgehead substitution. With relative electronegativities of $\text{Me}_3\text{Sn} < \text{Me}_3\text{Si} < \text{H}_3\text{Si} < \text{CH}_3 < \text{H}$ it is not surprising that methyl substitution leads to a decrease in $E(5) - E(1)$. When back-lobe factors are included, silyl (SiH₃) substitution may well destabilize the parent (**1**) less than methyl substitution; the favorable orbital interactions mentioned previously would serve to oppose this effect in the cation as well as the unfavorable

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polar-field influence with an overall decrease in relative energy ($E(5) - E(1)$) with respect to the norbornyl system ($X = H$). When further metalloids substituents (SiMe_3 , SnMe_3) are included, the favorable orbital interactions in the cations (**5**) dominate, leading to reductions in the calculated energy separations and hence increases in rates of solvolysis of the corresponding triflates. Interestingly, the calculated (MP2/6-31G*) weak stabilizing influence of the 3-methyl group in the bicyclo[1.1.1]pent-1-yl cation (relative hydride affinity = -1.0 kcal/mol)²⁹ is not in accord with the significant decelerating effects (10–20-fold) of this group on the solvolysis rates of the bicyclo[1.1.1]pent-1-yl bromides²⁸ and iodides.²⁹ This discordant result may be due to anchimeric assistance in the solvolysis of the parent substrate as a consequence of nucleophilic participation by the solvent at 3-H.²⁸

Earlier on in the discussion we drew attention to the Arrhenius eqs 1 and 3 which indicate that the parent and silicon compounds (**1**, $Y = \text{OSO}_2\text{CF}_3$; $X = H$ and SiMe_3) have similar activation energies (E_a). Taken at face value, this implies that the origin of the significant rate enhancement ($\text{Me}_3\text{Si}/H = 78$ (80E)) is entropic! However, in the light of the large calculated stabilizing influence of SiMe_3 in **5** (11.1 kcal mol⁻¹, see Table 4) we believe that an interplay of external and internal enthalpy effects as well as entropy effects, which are not well understood, are probably responsible for the unusual kinetic observation. It is of interest to note that situations of this kind have been referred to as isenthalpic relationships by Hammett.³⁷ To the best of our knowledge such relationships are unprecedented for carbocation mediated reactions. Clearly further solvent and temperature dependence studies on the solvolysis rates of **1** ($Y = \text{OSO}_2\text{CF}_3$; $X = H$, SiMe_3 , and SnMe_3) are necessary in order to make sense of the situation. One question that comes to mind is "what is the extent of nucleophilic participation by the solvent at the oxophilic Si center in the transition state?"

Finally, we wish to emphasize that the revelation from this study that the electronic effects of SiMe_3 and SnMe_3 are much more pronounced in **5** compared to **4** seemingly suggests that back-lobe through-space interactions are finely tuned with respect to internuclear distance and interorbital angles. However, the fact that the adamantane molecular skeleton is considerably less strained than that of norbornane and, therefore, presumably more amenable to structural adjustment to allow maximization of the back-lobe interaction raises the question that electron demand may be the overriding factor. The vacant bridgehead orbital in the 1-adamantyl cation is optimally aligned with three C–C bonds for maximum hyperconjugative dispersal of the electron deficiency.^{9,38} Consequently, very little demand is placed on the homohyperconjugative abilities of the C–Si and C–Sn bonds in **4**. By contrast, the electron deficiency in the 1-norbornyl cation is essentially localized on the bridgehead carbon as a result of poorly aligned C–C bonds being ineffectual at hyperconjugation. Thus, electron demand on the corresponding C–M bonds in **5** is necessarily very high.

Experimental Section

General. Melting and boiling points are uncorrected. Liquid samples were purified by distillation on a Kugelrohr apparatus (Büchi, GKR-50). Hence, boiling points quoted pertain to this instrument. Analytical vapor-phase chromatographic (VPC) analyses were performed on a Perkin Elmer Auto system gas chromatograph with FID using a 25-m capillary column (Alltech RSL-150, 0.32 mm column). NMR spectra were recorded on a Varian Gemini-300 spectrometer

operating at 300.75 (¹H), 282.328 (¹⁹F), 111.9 (¹¹⁹Sn), and 75.46 MHz (¹³C). Routine ¹H NMR spectra were measured with a Hitachi RR-1200 (60 MHz). Mass spectra and high-resolution mass spectra (HRMS) were recorded on a Kratos MS25RF spectrometer. GC-MS analyses were run on a Varian Saturn 4D instrument (column: 30 m, 0.22 mm, 0.25 μm film thickness; 5% phenylmethylpolysiloxane as stationary phase with helium (15 psi) as the carrier gas).

Ethanol was refluxed over magnesium ethoxide and distilled. 2,2,2-Trifluoroethanol was stored over 4A molecular sieves and distilled.

1-Bromo-4-methoxybicyclo[2.2.1]heptane (1: X = Br, Y = OCH₃). Following procedures recently described for the preparation of 1-bromo-3-chloroadamantane (**3**: $X = \text{Cl}$, $Y = \text{Br}$) from 3-chloroadamantane-1-carboxylic acid,³⁹ 4-methoxybicyclo[2.2.1]heptane-1-carboxylic acid⁴⁰ (**1**: $X = \text{COOH}$, $Y = \text{OCH}_3$; 7.28 g, 42.82 mmol) was converted into the title compound. Kugelrohr distillation (67–75 °C/15mm) afforded the methoxy bromide as a colorless oil (7.39 g, 85%): ¹H NMR (CDCl_3) δ 1.60–1.69 (2H, m), 1.90–2.28 (8H, m), 3.29 (3H, s); ¹³C NMR (CDCl_3) δ 83.28, 57.99, 52.59, 48.97, 40.45, 33.44; HRMS (EI) calcd for $\text{C}_8\text{H}_{13}\text{OBr}$ 204.0150/206.0131, found 176.9739/174.9759 ($M^+ - \text{C}_2\text{H}_5$; 2%, 2%), calcd for ($M^+ - \text{C}_2\text{H}_5$) 176.9766/174.9780, found 125.0981 ($M^+ - \text{Br}$, 100%), calcd for ($M^+ - \text{Br}$) 125.0966.

4-Bromobicyclo[2.2.1]heptan-1-ol (1: X = Br, Y = OH). A mixture of the methoxy bromide (**1**: $X = \text{Br}$, $Y = \text{OCH}_3$; 5 g, 24.4 mmol), 48% aqueous hydrobromic acid (25 g), and acetic anhydride (25 g) was refluxed under a nitrogen atmosphere for 24 h. The solution was cooled, poured onto ice (ca. 100 g), and stirred for 2 h before being saturated with salt and then extracted with ether (3 × 50 mL). The combined ether extracts were washed with a saturated aqueous sodium bicarbonate solution before drying over sodium sulfate. Removal of the solvent in vacuum afforded a solid which sublimed to give the title compound as a white solid (4.46 g, 96%). Recrystallization from a mixture of hexane/ethanol gave white crystals: mp 83–85 °C; ¹H NMR (CDCl_3) δ 1.70–1.78 (2H, m), 1.82–1.93 (2H, m), 1.97 (1H, s), 2.03–2.13 (4H, m), 2.17–2.31 (2H, m); ¹³C NMR (CDCl_3) δ 78.76, 58.00, 52.71, 40.81, 37.52; HRMS (EI) calcd for $\text{C}_7\text{H}_{11}\text{OBr}$ 189.9994/191.9974, found 162.9579/160.9596 ($M^+ - \text{C}_2\text{H}_5$; 1.7%, 1.8%), calcd for ($M^+ - \text{C}_2\text{H}_5$) 162.9583/160.9603, found 111.0826 ($M^+ - \text{Br}$, 100%), calcd for ($M^+ - \text{Br}$) 111.0809.

1-Bromo-4-(trimethylsilyloxy)bicyclo[2.2.1]heptane (1: X = Br, Y = OSi(CH₃)₃). By use of the procedure of Strating et al.,⁴¹ freshly distilled chlorotrimethylsilane (2.7 mL, 21.71 mmol) was slowly added to a well-stirred solution of the bromo alcohol (**1**: $X = \text{Br}$, $Y = \text{OH}$; 3.95 g, 20.68 mmol) in anhydrous pyridine (4 mL) and allowed to stir overnight at ambient temperature. The reaction mixture was then taken up into hexane and washed successively with aqueous sodium bicarbonate, cold dilute hydrochloric acid (1.5 M), and aqueous sodium bicarbonate before drying over sodium sulfate. Removal of the solvent in vacuum gave a colorless oil (5.4 g, 99%) which was distilled (70 °C/0.2 mm) to give the title compound. ¹H NMR (CDCl_3) δ 0.12 (9H, s), 1.66–1.75 (2H, m), 1.81–1.93 (2H, m), 1.99–2.08 (4H, m), 2.14–2.25 (2H, m); ¹³C NMR (CDCl_3) δ 79.81, 58.11, 52.76, 40.77, 38.20, 1.89; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{19}\text{OSiBr}$ 262.0389/264.0369, found 162.9587/160.9579 ($M^+ - \text{C}_5\text{H}_{13}\text{Si}$; 2.1%, 1.1%), calcd for ($M^+ - \text{C}_5\text{H}_{13}\text{Si}$) 162.9583/160.9603, found 111.0817 ($M^+ - \text{C}_3\text{H}_8\text{SiBr}$, 100%), calcd for ($M^+ - \text{C}_3\text{H}_8\text{SiBr}$) 111.0809.

4-(Trimethylsilyl)bicyclo[2.2.1]heptan-1-ol (1: X = Si(CH₃)₃, Y = OH). By use of a procedure outlined by Shippey and Dervan,⁴² a solution of (trimethylsilyl)sodium was prepared by adding hexamethyldisilane (6.8 g, 46.4 mmol) dropwise to a well-stirred solution of freshly prepared sodium methoxide (5 g, 92.8 mmol) in dry hexamethylphosphoric triamide (HMPA; 65 mL) at room temperature under a nitrogen atmosphere. After the resulting red solution was stirred for 4 h, a solution of 1-bromo-4-(trimethylsilyloxy)bicyclo[2.2.1]heptane (**1**: $X = \text{Br}$, $Y = \text{OSi}(\text{CH}_3)_3$; 3.0 g, 11.6 mmol) in dry HMPA (3.5 mL) was then added dropwise over a period of ca. 10 min and the reaction mixture was then allowed to stand overnight with stirring. The

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mixture was then carefully quenched with a saturated aqueous ammonium chloride solution and then extracted thoroughly with pentane (3 × 100 mL). The combined extracts were dried over sodium sulfate and filtered, and the solvent was removed under vacuo to give the crude product. Kugelrohr distillation (55–65 °C/4mm) gave 1-(trimethylsilyl)-4-(trimethylsiloxy)bicyclo[2.2.1]heptane as a clear colorless oil (1.79 g, 60%) which was desilylated with tetrabutylammonium fluoride as previously described for similar bicyclo[2.2.2]octane derivatives.³ The crude product was distilled (75 °C/5mm) to give the title compound as a waxy white solid (1.09 g, 85%): mp 69–71 °C; ¹H NMR (CDCl₃) δ -0.025 (9H, s), 1.30–1.85 (11H, m); ¹³C NMR (CDCl₃) δ 84.67, 45.63, 36.28, 32.53, 31.84, -3.94; HRMS (EI) calcd for C₁₀H₂₀OSi 184.1283, found 184.1278 (M⁺, 14.5%).

4-(Trimethylstannyl)bicyclo[2.2.1]heptan-1-ol (1: X = Sn(CH₃)₃, Y = OH). 1-Bromo-4-(trimethylsiloxy)bicyclo[2.2.1]heptane (1: X = Br, Y = OSi(CH₃)₃; 2 g, 7.6 mmol) was stannylated and desilylated in exactly the same manner as previously described for the corresponding bicyclo[2.2.2]octane derivative.³ The crude product was sublimed (75 °C/0.1mm) to give the title compound as a white solid (890 mg, 64%): mp 79.5–81.5 °C; ¹H NMR (CDCl₃) δ -0.003 (9H, s, *J*_{Sn-H} = 49.93, 52.13 Hz), 1.41 (2H, s), 1.45–1.58 (4H, m), 1.58–1.70 (2H, m), 1.75–1.94 (2H, m), 2.47 (1H, s); ¹³C NMR (CDCl₃) δ 83.84 (*J*_{Sn-C} = 74.7 Hz), 47.57, 36.42 (*J*_{Sn-C} = 41 Hz), 34.99 (*J*_{Sn-C} = 11.1 Hz), 33.39, -11.99 (*J*_{Sn-C} = 303.1, 317.2 Hz); ¹¹⁹Sn NMR (CDCl₃, relative to Sn(CH₃)₄) δ 0.44; EIMS *m/z* (rel intensity) 276 (M⁺, 2.5), 261, 259, 257 (M⁺ - 15; 7.3, 6.9, 4.7), 165 (30.2), 135 (15.6), 111 (100), 93 (15.2); HMRS (EI) calcd for C₁₀H₂₀O₂Sn 276.0536, found 276.0545 (M⁺).

Preparation of Triflates of 1 (X = Si(CH₃)₃ and Sn(CH₃)₃; Y = OSO₂CF₃). By use of a general procedure,⁴³ triflic anhydride (65 μL, 0.38 mmol) was added dropwise to a well-stirred dichloromethane (1 mL) solution of the appropriate alcohol (1, Y = OH; 0.182 mmol) and pyridine (35 μL, 0.424 mmol) at -10 °C. The reaction mixture was then stirred at this temperature for 3 h before being quenched with iced water (5 mL) followed by successive washing of the dichloromethane extract with dilute hydrochloric acid (5%, 5 mL) and iced water (5 mL). After drying over sodium sulfate, the solvent was removed in vacuo to yield the crude triflate which was subsequently distilled. Boiling points, NMR, and mass spectroscopic data for the triflates (1, Y = OSO₂CF₃) are as follows: X = Si(CH₃)₃, bp 75 °C (1mm); ¹H NMR (CDCl₃) δ 0.005 (9H, s), 1.4–1.5 (2H, m), 1.81 (2H, s), 1.82–1.92 (2H, m), 1.95–2.15 (4H, m); ¹³C NMR (CDCl₃) δ 118.25 (q, *J*_{C-F} = 319.1 Hz), 102.67, 43.57, 33.78, 31.12, 30.04, -4.00; ¹⁹F NMR (CDCl₃, relative to FCl₃) δ 85.95; EIMS *m/z* (rel intensity) 301 (M⁺ - 15; 2.5), 183 (47.8), 77 (40.5), 73 (100); HRMS (EI) calcd for C₁₁H₁₉O₃SF₃Si 316.0776, found 301.0511 (M⁺ - CH₃), calcd for (M⁺ - CH₃) 301.0541; X = Sn(CH₃)₃, bp 75 °C (0.1mm); ¹H NMR (CDCl₃) δ 0.078 (9H, s, *J*_{Sn-H} = 50.79, 53.11 Hz), 1.56–1.67 (2H, m), 1.89–2.16 (8H, m); ¹³C NMR (CDCl₃) δ 118.26 (q, *J*_{C-F} = 319 Hz), 102.58 (*J*_{C-Sn} = 73.7 Hz), 46.47, 34.21 (*J*_{C-Sn} = 10 Hz), 34.13 (*J*_{C-Sn} = 39.2 Hz), 30.11, -11.81 (*J*_{C-Sn} = 314.3, 328.6 Hz); ¹⁹F NMR (CDCl₃, relative to FCl₃) δ 86.02; ¹¹⁹Sn NMR (CDCl₃, relative to Sn(CH₃)₄) δ 6.43; EIMS *m/z* (rel intensity) 393 (M⁺ - 15; 99.2), 164 (100), 134 (35.6), 111 (22.2), 94 (75.1), 78 (33.1); HRMS (EI) calcd for C₁₁H₁₉O₃SF₃Sn 408.0029, found 392.9823, 390.9836, 388.9851 (M⁺ - CH₃; 63.3%, 50.2%, 29.9%), calcd for (M⁺ - CH₃) 392.9794, 390.9790, 388.9793.

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Kinetic Movements. The solvolysis rates (see Table 1) in 80 vol % aqueous ethanol (80E) and 97% w/w aqueous trifluoroethanol (97T), both containing 0.05 M 2,6-lutidine, were measured using recently published ¹⁹F and ¹H NMR methodologies,^{44,45} respectively.

Product Determination. The products of solvolysis of the triflates (1, Y = OSO₂CF₃) were determined by GC-MS and VPC analyses of the spent solutions from the NMR kinetic measurements. The analyses were facilitated by the availability of authentic samples of the alcohols (1, Y = OH; X = H, Si(CH₃)₃, and Sn(CH₃)₃). Only direct substitution products were identified (see Table 3). For the silyl and stannyl triflates, no evidence of desilylation and destannylation products (Me₃MOR; M = Si and Sn) could be found. The GC-MS *m/e* (rel intensity) data of the product mixtures are as follows: X = H (80E), 112 (M⁺, 1), 111 (M⁺ - 1, 2), 97 (24), 95 (25), 83 (100), 79 (8), 70 (36), 67 (11), 65 (6); 140 (M⁺, 1), 139 (M⁺ - 1, 3), 125 (3), 111 (42), 97 (14), 83 (100), 79 (11), 70 (10), 67 (16). X = CH₃ (80E), 126 (M⁺, 0.5), 125 (2), 110 (8), 97 (100), 84 (5), 79 (3), 66 (6); 154 (M⁺, 2), 153 (M⁺ - 1, 5), 139 (4), 125 (100), 111 (7), 97 (50), 84 (6), 79 (4), 65 (3). X = Si(CH₃)₃ (80E), 184 (M⁺, 2), 183 (M⁺ - 1, 3), 169 (48), 95 (20), 83 (16), 79 (30), 75 (50), 73 (100), 67 (6); 212 (M⁺, 1), 211 (M⁺ - 1, 2), 197 (10), 183 (48), 155 (14), 139 (10), 111 (20), 94 (50), 79 (35), 73 (100). X = Sn(CH₃)₃ (80E), 276 (M⁺, 1), 274 (2), 261 (50), 243 (12), 215 (4), 165 (28), 135 (30), 111 (52), 93 (100), 83 (33), 67 (20); 304 (M⁺, 2), 302 (3), 287 (60), 243 (12), 165 (4), 139 (100), 111 (72), 93 (100), 81 (50), 67 (20). X = H (97T), 112 (M⁺, 1), 111 (M⁺ - 1, 3), 97 (12), 95 (12), 83 (100), 79 (4), 65 (8); 194 (M⁺, 1), 193 (M⁺ - 1, 2), 179 (8), 165 (100), 95 (5), 83 (10), 67 (8). X = CH₃ (97T), 125 (M⁺ - 1, 3), 111 (15), 97 (100), 79 (12), 70 (18); 208 (M⁺, 1), 207 (M⁺ - 1, 3), 193 (14), 179 (100), 119 (99), 91 (90), 83 (20), 79 (30), 69 (15). X = Si(CH₃)₃ (97T), 265 (M⁺ - 1, 2), 251 (2), 237 (5), 192 (12), 183 (28), 93 (20), 79 (20), 73 (100), 67 (12). X = Sn(CH₃)₃ (97T), 343 (M⁺ - 15, 12), 273 (10), 243 (6), 193 (100), 165 (28), 93 (60), 77 (18), 67 (10).

Solutions of the silyl and stannyl triflate esters (ca. 0.1 M) in perdeuterated 97T, buffered with 2,6-lutidine, were also put in NMR tubes, capped, and allowed to stand at 50 °C until solvolysis was essentially complete, after which the ¹H and ¹³C NMR spectra were recorded. Resonances due to products of direct substitution were easily identified. No peaks for desilylation or destannylation products (Me₃MOR; M = Si and Sn) were evident. Furthermore, there was no evidence of possible fragmentation products (1,3-dimethylenecyclopentane). The ratios of the alcohol and ether products calculated from the integration of the spectra (X = Si(CH₃)₃, alcohol/ether = 22/78; X = Sn(CH₃)₃, alcohol/ether = 25/75) were similar to those determined by VPC (Table 3). ¹³C NMR data of product mixtures in perdeuterated 97T (rel Si(CH₃)₄): X = Si(CH₃)₃, δ 93.29, 43.12, 33.64, 32.91, 32.64, -3.87; 86.51, 46.24, 36.97, 34.11, 33.03, -3.81. X = Sn(CH₃)₃, δ 92.94 (*J*_{Sn-C} = 70.5 Hz), 45.08, 35.73 (*J*_{Sn-C} = 11.6 Hz), 33.95 (*J*_{Sn-C} = 42.1 Hz), 31.02, -12.48 (*J*_{Sn-C} = 327.7, 311.2 Hz); 85.99, 48.22, 37.23 (*J*_{Sn-C} = 41 Hz), 36.13 (11.6 Hz), 34.89, -12.48.

Acknowledgment. We are grateful to the Australian Research Council for partial financial support of this work. We thank Professor V. J. Shiner, Jr., for useful correspondence on some aspects of this study.

JA961870C

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