

Electrochemical Reduction of 3-(Trimethylstannyl)adamant-1-yl and 4-(Trimethylstannyl)bicyclo[2.2.2]oct-1-yl Bromides and Iodides

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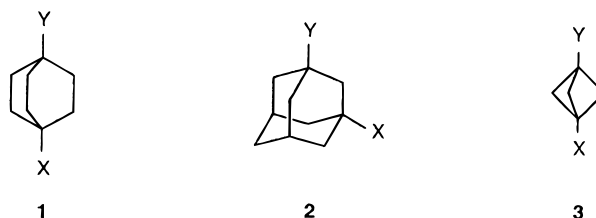
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Introduction

The effects of substituents on the stability of radicals continues to be a topic of much experimental and theoretical scrutiny.¹ Pertinent experimental parameters are homolytic bond dissociation energies (BDE) which provide direct information about stabilization energies of the corresponding radicals.² However, these parameters are not without a caveat since ground state energies, which can be difficult to assess, also have to be considered.³ A major hurdle has been the difficulty in directly measuring BDE values in relatively large organic molecules. Recent developments have circumvented this problem since cyclic voltammetry studies coupled with a newly developed dissociative electron-transfer model provides a convenient means of determining changes in the BDE value (ΔD) for the cleavage of a common nucleofuge, within series of structurally similar compounds.⁴

Application of the aforementioned electrochemical technique to series of dihalobicyclo[2.2.2]octanes (**1**), -adamantanes (**2**), and -bicyclo[1.1.1]pentanes (**3**) (Y = Br or I; X = F, Cl, Br, and I) has revealed substantial variations in the ΔD values of the first carbon-halogen bond to be cleaved.⁵ The variations are in the order I > Br > Cl > F. Moreover, the effects are much larger in series **2** and **3** than in **1**. These trends were readily rationalized in terms of through-space (adamantanes and bicyclooctanes) and through-bond (bicyclooctanes) sta-



bilizing interactions in the radical and, to a lesser extent, in the precursor dihalide.

Radical stabilization by the σ -electron-withdrawing halogens implies that the σ_{cx}^* orbital is of fundamental importance in saturated radical systems, i.e., σ -resonance acceptors are stabilizing. Interestingly, resonance stabilization energies of various π -acceptor and π -donor substituents determined from model system studies suggest that the most significant radical-stabilizing groups are those which are also good anion stabilizers.⁶ Thus, by analogy, it was of interest to determine the radical-stabilizing properties of a good σ -electron donor substituent (e.g., $(\text{CH}_3)_3\text{Sn}$) in systems **1**, **2**, and **3** for comparison with the corresponding effects of the halogens. The possibility of significant stabilization of the bicyclo[2.2.2]oct-1-yl radical by a 4- $(\text{CH}_3)_3\text{Sn}$ group was proposed several years ago in connection with the trimethylstannylation of 1,4-dihalobicyclo[2.2.2]octanes (**1**, X = Y = halogens).⁷ More recently, EPR data for the 4-(trimethylstannyl)bicyclo[2.2.2]oct-1-yl radical strongly suggests the possibility of enhanced delocalization of the unpaired electron relative to the parent system.⁸

Herein, we report an extension of our electrochemical studies to appropriate tin-substituted derivatives of **1** and **2** (X = SnMe_3 ; Y = Cl, Br, and I). Unfortunately, because of synthetic difficulties we were unable to include the corresponding derivatives of **3** in our studies.⁹

Results and Discussion

The cyclic voltammograms of the iodo- and bromotin compounds of **1** and **2** were obtained in acetonitrile at a glassy carbon electrode. A single irreversible cathodic wave involving the exchange of two electrons per molecule was observed in all cases as previously shown for the parent systems (**1** and **2**, Y = I or Br and X = H).⁵ It should be noted that, like the parent chlorides,⁵ the chlorotin compounds of **1** and **2** (Y = Cl, X = SnMe_3) exhibited no reduction peak before the current rise due to the supporting electrolyte discharge.

Relevant information pertaining to the cyclic voltammograms and the dissociative electron-transfer model⁴ is summarized in Tables 1 and 2. It can be seen that the values of the transfer coefficient, α_{expl} , derived from either the peak width or from the slope of the E_p vs $\log v$ plots, are of the order of 0.3, i.e., considerably less than 0.5. Moreover, there is good agreement between these small experimental values and the theoretical value derived from the electron transfer model. Thus, the reductive cleavage behavior of the halotin derivatives of

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Table 1. Cyclic Voltammetric Characteristics of the Reduction of System 1^a

		X(1)-Y			
		I(1)-SnMe ₃	I(1)-H ⁿ	Br(1)-SnMe ₃	Br(1)-H ⁿ
electron/molecule		2.0	1.9	2.1	2.1
E_p (V vs SCE)	<i>b</i>	-2.17 ₅	-2.375	-2.62 ₅	-2.80
ϕ_r (mV)	<i>c</i>	-0.076	-0.078	-0.081	-0.083
$A10^{-4}$ (cm/s)	<i>d</i>	3.08	4.01	3.82	4.78
a (Å), e C (eV), f λ_o (eV)	<i>g</i>	3.06, 1.26, 1.029		2.83, 1.85, 1.113	
ΔG^\ddagger (eV)	<i>h</i>	0.385	0.392	0.391	0.396
$D_{X(1)-Y-Y(1)+X^-}$ (eV)	<i>i</i>	2.30	2.43	2.89	3.00
ΔD (meV)	<i>j</i>	132	0	112	0
$E_{X(1)-Y/Y(1)+X^-}^0$ (V vs SCE)	<i>k</i>	-1.04	-1.17	-1.04	-1.15
$\Delta G_{0,X(1)-Y/Y(1)+X^-}^\ddagger$ (eV)	<i>l</i>	0.83	0.86	1.00	1.02
α^{exptl} (from $E_{p/2} - E_p$)	<i>m</i>	0.31	0.29	0.29	0.31
α^{exptl} (from E_p vs log ν)		0.30	0.30		
α^{theor}		0.34	0.34	0.31	0.31

^a In acetonitrile + 0.1 M *n*-Bu₄NBF₄ at a glassy carbon electrode at 20 °C. ^b Peak potential at 0.1 V/S. ^c Potential difference between the reaction site and the solution. ^d Preexponential factor. ^e Equivalent hard-sphere radius. ^f $C = E_{X(1)-Y/Y(1)+X^-}^0 + D_{X(1)-Y-Y(1)+X^-}$. ^g Solvent reorganization energy. ^h Activation free energy. ⁱ Bond dissociation energy. ^j $\Delta D = D_{X(1)-H-H(1)+X^-} - D_{X(1)-Y-Y(1)+X^-}$. ^k Standard potential of the reaction. ^l Intrinsic barrier free energy. ^m Transfer coefficient. ⁿ Taken from ref 5.

Table 2. Cyclic Voltammetric Characteristics of the Reduction of System 2^a

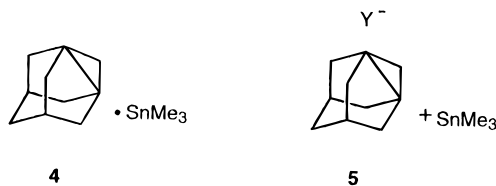
		X(2)-Y			
		I(2)-SnMe ₃	I(2)-H ⁿ	Br(2)-SnMe ₃	Br(2)-H ⁿ
electron/molecule		2.0	2.1	2.0	2.1
E_p (V vs SCE)	<i>b</i>	2.095	-2.20	-2.525	-2.70
ϕ_r (mV)	<i>c</i>	-0.075	-0.076	-0.080	-0.082
$A10^{-4}$ (cm/s)	<i>d</i>	3.09	3.81	3.82	4.20
a (Å), e C (eV), f λ_o (eV)	<i>g</i>	3.06, 1.26, 1.029		2.83, 1.85, 1.113	
ΔG^\ddagger (eV)	<i>h</i>	0.385	0.391	0.391	0.393
$D_{X(2)-Y-Y(2)+X^-}$ (eV)	<i>i</i>	2.25	2.32	2.82	2.94
ΔD (meV)	<i>j</i>	7 ₃	0	116	0
$E_{X(2)-Y/Y(2)+X^-}^0$ (V vs SCE)	<i>k</i>	-0.99	-1.06	-0.97	-1.09
$\Delta G_{0,X(2)-Y/Y(2)+X^-}^\ddagger$ (eV)	<i>l</i>	0.82	0.84	0.98	1.01
α^{exptl} (from $E_{p/2} - E_p$)	<i>m</i>	0.29	0.29	0.29	0.29
α^{exptl} (from E_p vs log ν)		0.31	0.30		
α^{theor}		0.34	0.34	0.31	0.31

^a In acetonitrile + 0.1 M *n*-Bu₄NBF₄ at a glassy carbon electrode at 20 °C. ^b Peak potential at 0.1 V/S. ^c Potential difference between the reaction site and the solution. ^d Preexponential factor. ^e Equivalent hard-sphere radius. ^f $C = E_{X(2)-Y/Y(2)+X^-}^0 + D_{X(2)-Y-Y(2)+X^-}$. ^g Solvent reorganization energy. ^h Activation free energy. ⁱ Bond dissociation energy. ^j $\Delta D = D_{X(2)-H-H(2)+X^-} - D_{X(2)-Y-Y(2)+X^-}$. ^k Standard potential of the reaction. ^l Intrinsic barrier free energy. ^m Transfer coefficient. ⁿ Taken from ref 5.

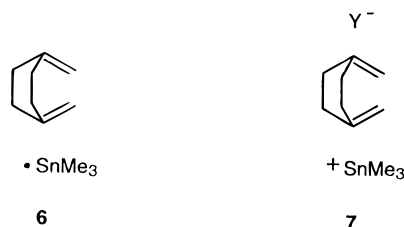
1 and **2** is similar to that previously noted for the parent compounds,⁵ namely, that a concerted mechanism is followed rather than a pathway involving the formation of an anion radical. Similar observations have been reported in studies on the electrochemical reduction of simple saturated halides.⁴

Further scrutiny of Tables 1 and 2 reveals that there is a definite **positive** shift of the peak potential of the bromides and iodides of both systems on changing the substituent from H to SnMe₃.¹⁰ It should be noted that a similar trend was previously observed for the halogen substituents.⁵ By application of the appropriate equations of the dissociative electron transfer model,⁴ these perturbations of the reduction potential translate to values for the weakening of the C–Br or C–I bond dissociation energy, ΔD values (Tables 1 and 2), upon SnMe₃ substitution. A most noticeable and surprising result is that the relative magnitude of the ΔD variations for SnMe₃ in **1** and **2** (**1** > **2**) is *opposite* to what was found for the halogen substituents (**2** > **1**; Cl, Br, and I).⁵

Moreover, the ΔD values for SnMe₃ are larger than those for the halogens (Cl, Br, and I) in **1** but significantly smaller than those for the same substituents in **2**. A possible rationalization of these unexpected trends can be advanced based on the idea that in **2** through-space stabilization involving the C–Sn bond is strong in both the radical and the starting molecule (depicted by canonical structures **4** and **5**, respectively), whereas in



1, through-bond stabilization is strong in the radical but not in the halide precursor (depicted by canonical structures **6** and **7**, respectively).



(10) (a) It is of interest to note that the polarographic half-wave reduction potential on mercury (in DMF containing *n*-Bu₄NClO₄) of 1-iodo-4-(trimethylstannyl)bicyclo[2.2.2]octane (**1**, X = SnMe₃, Y = I) is, within experimental error, identical to the parent compound (**1**, X = H, Y = I).^{10b} However, on changing the supporting electrolyte to Me₄NClO₄ the $E_{1/2}$ value of the former compound (-1.84V) is significantly more *positive* than the value for the parent system (-1.97V). These results highlight the difficulty of relating the variations of the $E_{1/2}$ values on Hg to intrinsic properties of the molecules.^{10c} (b) Adcock, W.; Kok, G. B.; Iyer, V. S.; Peters, D. G.; Lundy, K. M. *J. Org. Chem.* **1986**, *51*, 564–567. (c) See ref 15a of ref 5.

Table 3. ^{119}Sn Substituent Chemical Shifts (SCS) and One-Bond Carbon–Tin Coupling Constants ($^1J(^{13}\text{C}, ^{119}\text{Sn})$) for **1** and **2** ($\text{Y} = \text{SnMe}_3$)^a

X	σ_{F}^b	^{119}Sn SCS, ^c ppm		$^1J(^{13}\text{C}, ^{119}\text{Sn})$, ^{d,e} Hz		$^1J(^{13}\text{CH}_3, ^{119}\text{Sn})$, ^d Hz	
		1 ^f	2 ^g	1 ^f	2 ^g	1 ^f	2 ^g
H	0.00	0.00	0.00	474 (0.0)	455 (0.0) ^h	297 (0.0)	291 (0.0) ^h
F	0.42	11.67	8.15	441 (−33.0)	433 (−22.0) ^h	308 (11.0)	304 (13.0) ^h
Cl	0.43	10.35	8.44	443 (−31.0)	424 (−31.0)	308 (11.0)	304 (13.0)
Br	0.44	11.67	7.82	442 (−32.0) ^g	417 (−38.0)	308 (11.0) ^g	304 (13.0)
I	0.43	14.08	4.79	444 (−30.0) ^g	416 (−39.0)	308 (11.0) ^g	303 (12.0)
SnMe ₃	0.02	−5.53	−1.13	478 (4.0)	441 (−14.0)	297 (0.0)	289 (−2.0)

^a Solvent, CDCl₃. ^b Taken from ref 26. ^c Chemical shifts (ppm) relative to shifts of parent systems **1** and **2**, X = H (relative to internal SnMe₄): 0.46 and −6.47 ppm, respectively. Accurate to ±0.1 ppm. Downfield shifts are positive. ^d Measured from ¹³C NMR spectra. ^e $^1J(^{13}\text{C}_4, ^{119}\text{Sn})$ for **1** and $^1J(^{13}\text{C}_3, ^{119}\text{Sn})$ for **2**. ^f Taken from ref 11. ^g This study. ^h Measured from ¹¹⁹Sn NMR spectra.

However, a systematic study of NMR parameters which are particularly sensitive to interactions involving the C–Sn bond (^{119}Sn substituent chemical shifts (SCS) and one-bond carbon–tin coupling constants ($^1J(^{13}\text{C}, ^{119}\text{Sn})$) clearly suggest that electron delocalization via double hyperconjugation (depicted by structure **7**) is a significant stabilizing factor in the neutral ground state of **1** ($\text{Y} = \text{SnMe}_3$, X = halogen).¹¹ Although these particular parameters cannot be deployed to establish the energy equivalence of this perturbation, they do provide a convenient means of assessing electronic phenomena in the ground state. Consequently, in an attempt to evaluate the relative importance of through-space effects in the ground state of **2** ($\text{Y} = \text{SnMe}_3$) we have measured the ^{119}Sn SCS and $^1J(^{13}\text{C}, ^{119}\text{Sn})$ parameters of the halogen and tin substituents for this system. These are listed in Table 3 together with the known corresponding data of **1** ($\text{Y} = \text{SnMe}_3$).¹¹ Previously, factorization of the SCS of **1** ($\text{Y} = \text{SnMe}_3$) into polar field ($\rho_{\text{F}}\sigma_{\text{F}}$; $\rho_{\text{F}} = 7.00(\text{CDCl}_3)$) and residual contributions ($\text{SCS} - \rho_{\text{F}}\sigma_{\text{F}}$) revealed that the dominant factor regulating the shifts of this system is through-bond electron delocalization. This was subsequently confirmed by model system studies.¹² Although data are not available to allow a similar analysis of the SCS of **2** ($\text{Y} = \text{SnMe}_3$), angle and distance considerations suggest that the polar field term ($\rho_{\text{F}}\sigma_{\text{F}}$) should be approximately the same for **1** and **2** ($\text{Y} = \text{SnMe}_3$). Thus, taken at face value the relative magnitude of the residuals ($\text{SCS} - \rho_{\text{F}}\sigma_{\text{F}}$) of **1** and **2** ($\text{Y} = \text{SnMe}_3$) suggest that through-bond effects in the former are more important than through-space effects in the latter. However, because the SCS of **2** ($\text{Y} = \text{SnMe}_3$) probably embody 1,3-nonbonded repulsion influences¹³ as well as unusual antagonistic through-two-bond effects of the kind observed for the corresponding 4-substituted bicyclo[2.2.1]hept-1-yltrimethylstannanes,¹¹ this assessment may be questionable. Perhaps more reliable parameters to interpret are the $^1J(^{13}\text{C}, ^{119}\text{Sn})$ values which are directly related to the bond order of the C–Sn bond.¹⁴ Structures **5** and **7** imply that through-space and through-bond effects in **2** and **1** ($\text{Y} = \text{SnMe}_3$), respectively, should significantly decrease the bond order of the C–Sn bond and, therefore, decrease the appropriate coupling constants. It can be seen (Table 3) that the $^1J(^{13}\text{C}_4, ^{119}\text{Sn})$ and $^1J(^{13}\text{C}_3, ^{119}\text{Sn})$ values of the halogens in both **1** and **2**

($\text{Y} = \text{SnMe}_3$), respectively, are significantly less than the corresponding values of the respective parent system (X = H). Although some of the variation must be ascribed to a redistribution of s character in the binding Sn hybrid orbitals in response to an electrostatic field polarizing influence,^{11,15} $^1J(^{13}\text{CH}_3, ^{119}\text{Sn})$ values increase in accord with the σ_{F} values (Table 3), the importance of stabilizing electronic delocalization effects in the neutral ground state of both systems appears to be substantiated. It is of interest to note that $\Sigma J(\text{Hz})$ about Sn is fairly constant in both series, **1** ($\text{Y} = \text{SnMe}_3$; 1365 ± 5 Hz) and **2** ($\text{Y} = \text{SnMe}_3$; 1328 ± 10 Hz), except for the F and SnMe₃ derivatives of the latter system (1345 and 1308 Hz, respectively). Hence, besides hybridization changes at the Sn atom there must also be significant structural changes at the adjacent bridgehead carbon for these two compounds. This is probably in response to substituent-induced variations in the 1,3-nonbonded repulsion term by the very electronegative and electropositive groups (F and SnMe₃, respectively).¹³

In the light of the aforementioned NMR evidence it seems reasonable to conclude then that the ΔD values of the bromides and iodides of **1** and **2** (Tables 1 and 2) provide minimal estimates of the order of magnitude of through-bond and through-space stabilizing interactions (structures **6** and **4**, respectively) in the tin-substituted radical species. Although the apparent larger effect of the former interaction compared to the latter is somewhat surprising in view of the corresponding results for the halogen substituents,⁵ it is worth noting that the 1,3-through-space interaction (γ -effect; homohyperconjugation) between the C–Sn bond and the empty orbital in the 3-(trimethylstannyl)adamant-1-yl cation¹⁶ is considerably weaker than the corresponding through-bond coupling (δ -effect; double hyperconjugation) in the 4-(trimethylstannyl)bicyclo[2.2.2]oct-1-yl cation.^{17,18} Thus, it appears that through-space interactions are finely tuned with respect to the degree of back-lobe orbital extension of the substrate-substituent bond and, as well,

(15) Further evidence for this view is found in the observation that for 10-bromo-9-(trimethylstannyl)tritycene, a system in which through-bond electron delocalization is effectively precluded, both $^1J_{\text{C-Sn}}$ values (Hz) are significantly different from those in the parent system (340.6, 401.0 versus 336.9, 407.7, respectively).¹² However, these electrostatic field-induced perturbations are significantly less than the corresponding influences in the bicyclo[2.2.2]octane system (see Table 3, system 1, X = Br).

(16) Fischer, W.; Grob, C. A. *Helv. Chim. Acta.* **1978**, *61*, 1588–1608.

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(18) A study of the solvolytic reactivity of 3-substituted (X) 1-bromoadamantanes (**2**, Y = Br) in 80% aqueous ethanol reveals a rate enhancement of 58 for X = SnMe₃.¹⁶ A much larger rate acceleration ($\times 781$) is observed for this group in the solvolysis of 4-substituted (X) bicyclo[2.2.2]octyl mesylates (**1**, Y = OSO₂CH₃) in the same solvent mixture.¹⁷

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to the susceptibility of the substrate to undergo necessary structural adjustments for optimization of the interaction to occur.

Experimental Section

General. Instrumentation deployed was as previously described.¹⁹

Cyclic Voltammetry. The cyclic voltammograms were obtained as previously described.⁵

Chemicals. Acetonitrile (Merck Uvasol) and the supporting electrolyte, *n*-Bu₄BF₄ (Fluka, puriss), were used as received.

Compounds. 1-Fluoro-3-(trimethylstannyl)adamantane,²⁰ 1-(trimethylstannyl)adamantane,²⁰ 1,3-bis(trimethylstannyl)adamantane,²⁰ and 1-chloro-4-(trimethylstannyl)bicyclo[2.2.2]octane¹¹ were available from other studies. 1-Chloro-, 1-bromo-, and 1-iodo-3-(trimethylstannyl)adamantane were prepared as previously described.²⁰

4-(Trimethylstannyl)bicyclo[2.2.2]octane-1-carboxylic Acid (1, X = SnMe₃, Y = COOH). By use of the procedure of Brown et al.,²¹ a solution of 4-iodobicyclo[2.2.2]octane-1-carboxylic acid (20 g, 71.40 mmol)²² in dry tetrahydrofuran (190 mL) was treated dropwise with borane–methyl sulfide (2.5 mol equiv), and the resulting mixture was allowed to stir overnight under a nitrogen atmosphere. Methanol (100–120 mL) was then carefully added to the reaction mixture, and the resulting solution was then heated under reflux for 1 h. The residue obtained after removal of the solvent under vacuum was then further treated with sodium methoxide in methanol (500 mL) under reflux to effect complete hydrolysis of the intermediate borate complex. After removal of the solvent in vacuo the residue was extracted with diethyl ether and the combined extracts washed with water. After drying (MgSO₄), the solvent was removed in vacuo to afford 1-(hydroxymethyl)-4-iodobicyclo[2.2.2]octane which, after sublimation, afforded a white solid (18.0g, 95%): mp 76–78 °C, ¹H NMR (CDCl₃) δ 1.35 (1H, bs, OH), 1.38–2.71 (12H, m), 3.20 (2H, s).

By use of the procedure of Strating et al.,²³ freshly distilled chlorotrimethylsilane (5.4 g, 50.0 mmol) was added dropwise to a well-stirred solution of 1-(hydroxymethyl)-4-iodobicyclo[2.2.2]octane (10 g, 37.7 mmol) in anhydrous pyridine (45 mL) under an atmosphere of nitrogen. The reaction mixture was then refluxed for 1 h before being allowed to stir overnight at ambient temperature. Following workup as prescribed by Strating et al.,²³ the crude silyl ether was distilled (130 °C/0.1 mm) to afford a white solid (12.32 g, 97%): mp 39–41 °C; ¹H NMR (CDCl₃) δ 0.00 (9H, s), 1.37–2.70 (12H, m), 3.12 (2H, s).

A solution of the iodosilyl ether (11 g, 32.64 mmol) in anhydrous THF (55 mL) was added dropwise to a well-stirred solution of (trimethylstannyl)lithium (130.56 mmol) in anhydrous THF (100 mL)²⁴ at 0 °C under a nitrogen atmosphere. The mixture was then stirred at room temperature for 4 days before being quenched with a saturated aqueous solution of ammonium chloride. A standard workup afforded a crude mixture of 1-(hydroxymethyl)-4-(trimethylstannyl)bicyclo[2.2.2]octane (97%) and 1-(hydroxymethyl)bicyclo[2.2.2]octane (3%). Fractional Kugel-

rohr distillation (125 °C/0 mm) gave the former compound as a slightly impure white solid (9 g; 90%): ¹H NMR (CDCl₃) δ –0.04 (9H, s, *J*_{SnH} = 48.3 and 50.6 Hz), 1.14 (1H, t, *J*_{HH} = 6.15 Hz), 1.32–1.78 (12H, m), 3.19 (2H, d, *J*_{HH} = 6.11 Hz); ¹³C NMR (CDCl₃) δ 71.97 (*J*_{SnC} = 11.72 Hz), 31.95 (*J*_{SnC} = 2.93 Hz), 29.89, 28.89 (*J*_{SnC} = 53.71 and 56.64 Hz), 22.28 (*J*_{SnC} = 444.3 and 464.8 Hz), –12.63 (*J*_{SnC} = 286.6 and 300.3 Hz).

A solution of Jones reagent²⁵ (H₂O (10 mL), H₂SO₄ (2.52 mL), and CrO₃ (3.06 g, 30.64 mmol)) was added dropwise by perfusor to a well-stirred solution of 1-(hydroxymethyl)-4-(trimethylstannyl)bicyclo[2.2.2]octane (2.6 g, 8.59 mmol) in acetone (200 mL) until the initial blue-green color of the reaction mixture had changed to a distinct orange yellow appearance. A large volume of dichloromethane (ca. 400 mL) was added, and the chromium salts were removed by filtration. After the mixture was washed with water and dried (MgSO₄), the solvent was removed in vacuo to afford the crude acid. Recrystallization from chloroform gave the title compound (2.61 g, 96%) as white platelets: mp 240–242 °C; ¹H NMR (CDCl₃) δ 0.0 (9H, s, *J*_{SnH} = 48.96 and 51.24 Hz), 1.77 (12H, s), 9.36 (1H, bs); ¹³C NMR (CDCl₃) δ 184.4, 37.69, 29.50, 28.86 (*J*_{SnC} = 53.8 Hz), 20.70, –12.50 (*J*_{SnC} = 290.9 and 304.6 Hz). Anal. Calcd for C₁₂H₂₂SnO₂: C, 45.47; H, 7.00. Found: C, 45.60; H, 7.10.

1-Bromo-4-(trimethylstannyl)bicyclo[2.2.2]octane (1, X = SnMe₃, Y = Br). Following procedures recently described for the preparation of 1-bromo-3-chloroadamantane (**2**, X = Cl, Y = Br) from 3-chloroadamantane-1-carboxylic acid,²⁰ 4-(trimethylstannyl)bicyclo[2.2.2]octane-1-carboxylic acid (**1**, X = SnMe₃, Y = COOH; 2 g, 6.32 mmol) was converted into the title compound. Column chromatography (basic alumina; hexane as eluent) followed by recrystallization from absolute ethanol afforded the tin bromide (**1**, X = SnMe₃, Y = Br) as white crystals (1.77 g, 77%): mp 78–79 °C; ¹H NMR (CDCl₃) δ –0.02 (9H, s, *J*_{SnH} = 48.84 and 51.24 Hz), 1.71–2.46 (12H, m); ¹³C NMR (CDCl₃) δ 65.99, 38.67 (*J*_{SnC} = 53.85 Hz), 33.39, 20.12, –12.41 (*J*_{SnC} = 294.8 and 308.3 Hz). Anal. Calcd for C₁₁H₂₁SnBr: C, 37.55; H, 6.02. Found: C, 37.60; H, 5.80.

1-Iodo-4-(trimethylstannyl)bicyclo[2.2.2]octane (1, X = SnMe₃, Y = I). Following procedures recently described for the preparation of 1-chloro-3-iodoadamantane (**2**, X = Cl, Y = I) from 3-chloroadamantane-1-carboxylic acid,²⁰ 4-(trimethylstannyl)bicyclo[2.2.2]octane-1-carboxylic acid (**1**, X = SnMe₃, Y = COOH; 2 g, 6.32 mmol) was converted into the title compound. Column chromatography (basic alumina; hexane as solvent) followed by sublimation (70 °C/0.01 mm) and recrystallization (4 × 1) from an ethanol/pentane mixture (9:1) afforded the tin iodide (**1**, X = SnMe₃, Y = I) as white crystals (1.73 g, 69%): mp 113–114 °C (lit.^{10b} mp 88–89 °C); ¹H NMR (CDCl₃) δ 0.00 (9H, s, *J*_{SnH} = 48.96 and 51.00 Hz), 1.74–2.80 (12H, m); ¹³C NMR (CDCl₃) δ 49.03, 41.57 (*J*_{SnC} = 52.50 Hz), 33.92, 19.38, –12.53 (*J*_{SnC} = 294.3 and 308.0 Hz). Anal. Calcd for C₁₁H₂₁SnI: C, 33.12; H, 5.31. Found: C, 33.40; H, 5.30.

The aforementioned synthesis of the tin iodide is superior to a previously reported preparation which involves treatment of 1-fluoro-4-(trimethylstannyl)bicyclo[2.2.2]octane with iodotrimethylsilane in dichloromethane.^{10b} The latter reaction is capricious, and yields are low probably as a consequence of fragmentation of the intermediate 4-(trimethylstannyl)bicyclo[2.2.2]oct-1-yl cation.¹⁷

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