Mechanistic Definition of Trimethylstannylation of 1,3-Dihaloadamantanes: Delocalized Radical Anions as Possible Intermediates[1]

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A series of 1,3-dihaloadamantanes (3, X = Y = halogens) have been synthesized, characterized, and treated with (trimethylstannyl) alkali reagents (Me_3SnM, M = Li or Na) in the absence and presence of *tert*-butylamine (TBA) and dicyclohexylphosphine (DCPH). The product distributions of these reactions have been established by ^{13}C and ^{119}Sn NMR spectroscopy and vapor-phase chromatographic analyses. Tin substitution via an $S_{RN}1$-type pathway is shown to be a significant reaction for several of the derivatives of 3 (X = F, Y = Br or I; X = Cl, Y = Br or I; X = Y = Br) but not for the bromo iodide or diiodide (3, X = Br, Y = I and X = Y = I). For the latter two compounds, the formation of 1,3-dehydroadamantane or propellane 8 is the predominant reaction product while tin substitution is insignificant. Propellane 8 formation is also a significant reaction product for some of the other dihalo derivatives of 3 (X = Cl, Y = I and X = Y = Br) but not for others (3, X = F, Y = Br or I and X = Cl, Y = Br). The mechanism of formation of 8 is perplexing in light of the trapping experiments in the presence of TBA and DCPH. A possible pathway is proposed in which the key intermediate is a delocalized radical anion.

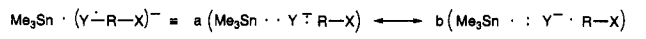
Introduction

In previous studies[2,3] we reported on the mechanism of trimethylstannylation of 1,4-dihalobicyclo[2.2.2]octanes 1 and -bicyclo[2.2.1]heptanes 2. For the former systems,[2]

1 2 3

a free radical chain process ($S_{RN}1$ like) appears to be the dominant if not the exclusive reaction pathway, while for the latter,[3] a polar mechanism initiated by the formation of a carbanion largely prevails but is in competition with a free radical route. One of the most salient features to emerge from the study of 2 is the fact that the competition between the radical and polar reaction pathways is delicately balanced. This fine tuning led us to propose that the transition state for both processes must be fairly similar and, therefore, that both mechanisms involve a single electron shift in the transition-state region. By use of the configuration mixing model (CM) developed by Pross, Shaik, and others,[4] a valence bond configurational description of the transition state for trimethylstannylation of bridgehead halopolycycloalkanes can be denoted as displayed in Scheme I. The relative magnitude of the weighting factors (a and b) governs the partitioning between the two mechanisms. Within the framework of this model, we[3] tentatively ascribed the observed substituent dependency of the mechanistic competition in 2 to homohyperconjugative electron delocalization (denoted by canonical structures 4 and 5 for system 2). This

Scheme I[a]



[a] R = polycyclic alkyl system; X = substitutent; Y = halogen leaving group.

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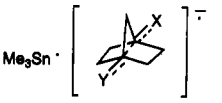
electronic interaction has the effect of increasing a relative to b, i.e. electron delocalization in the transition state (6) due to "back-lobe" orbital overlap ($\sigma_{CX}^* - \sigma_{CY}^*$). Recently,[5]



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some support for this idea has emerged from electron transmission spectroscopic studies of 2 (X = Y = Cl; X = Y = Br) which reveal significant 1,3-"through-space" intrabridgehead interactions between σ_{CX}^* and σ_{CY}^* in this model system.

In an attempt to provide further insight into the structural parameters governing the aforementioned phenomena, we decided to extend out studies to a series of 1,3-dihaloadamantanes 3 (X = F, Cl, Br, or I and Y = Br or I). A particularly pertinent feature of this model system is its structural semblance to both 1 and 2. On the one hand, it is similar to 2 with respective to the geometric relationship between the bridgehead groups. On the other,

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(1) Reported in part at the Toronto International Conference on Organic Reactive Intermediates (TICORI), Scarborough Campus, University of Toronto, Toronto, Canada, July 30–August 1, 1992.

(2) Adcock, W.; Iyer, V. S.; Kitching, W.; Young, D. *J. Org. Chem.* **1985**, *50*, 3706 and references cited therein.

(3) Adcock, W.; Gangodawila, H. *J. Org. Chem.* **1989**, *54*, 6040 and references cited therein.

(4) (a) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99 and references cited therein. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 198 and references cited therein.

(5) Huda, E.; Martin, H.-D.; Mayer, B.; Somnitz, K.-H.; Steigel, A.; Haddad, H.; Distefano, G.; Modelli, A. *Chem. Ber.* **1991**, *124*, 2879.

0022-3263/93/1958-7341$04.00/0

it is similar to 1 with respect to the s character in the exocyclic orbitals at the bridgehead position. Thus, PMO considerations[6] suggest that "back-lobe" orbital overlap interactions ($\sigma_{CX}^* - \sigma_{CY}^*$) should be larger in 3 than 2. Further impetus for us to explore the possibility of electron-transfer-induced competing polar and free radical reaction mechanisms in 3 is the earlier report of Kuivila et al.[7] that trimethylstannylation of 1-iodoadamantane partitions between two pathways (79% and 21% via radical and carbanion intermediates, respectively). Herein we report the results of our study.

Results and Discussion

1-Haloadamantanes 3 (X = H, Y = Halogen). By means of efficient free radical and carbanion trapping agents (dicyclohexylphosphine (DCPH) and *tert*-butylamine (TBA), respectively), Kuivila et al.[7] have claimed that trimethylstannylation of 1-bromo- and 1-iodoadamantane with Me_3SnNa in THF at 0 °C proceeds predominantly (100% and 79%, respectively) by a free radical process. We have corroborated the result for the bromo derivative but we have been unable to confirm the result for the iodo compound, namely, that 21% of the reaction occurs via a carbanion intermediate. We found that stannylation of 1-iodoadamantane with Me_3SnLi or Me_3SnNa in THF at 0 °C in the absence and presence of TBA leads essentially to the same product mixture (substitution (%)/reduction (%): 86/14 (Me_3SnLi), 92/8 (Me_3SnNa) and 83/17 (Me_3SnLi), 88/12 (Me_3SnNa), respectively). Thus, both 1-haloadamantanes appear to react exclusively via a free radical intermediate. Kuivila et al.[7] also reported that 1-chloroadamantane displays no reaction with Me_3SnNa in THF over a 10-day period at −4 °C. Our studies have confirmed the relatively unreactive nature of this compound in THF at 0 °C with Me_3SnLi or Me_3SnNa. However, slow trimethylstannylation does occur if the reaction mixture is allowed to warm to room temperature and to stand for several hours.

1,3-Dihaloadamantanes 3 (X = Y = Halogen). In preliminary studies we carried out trimethylstannylations of several 1,3-dihaloadamantanes 3 (X = F, Y = Br; X = Cl, Y = Br and I; X = Y = Br; X = Br, Y = I; and X = Y = I) in the manner previously described for 1[2] and 2[3]. This involved dropwise addition of Me_3SnLi (1 or 2 molar equiv; prepared directly from Me_3SnCl and Li in THF at 0 °C) to a THF solution of 3 maintained at 0 °C under N_2. After the reaction mixture was allowed to stir overnight at 0 °C, the reaction was carefully quenched with a saturated aqueous ammonium chloride solution followed by a standard workup. The product mixtures were examined by NMR (^{13}C and ^{119}Sn) and VPC but considerable difficulty was encountered in completely characterizing many of the mixtures. In particular, the bromo iodide and diiodide afforded complex mixtures as viscous syrupy liquids. The complexity of these reaction mixtures was highlighted by the extraordinary multitude of resonances in the respective ^{13}C NMR spectra. It proved impossible to fully characterize the mixtures from these spectra. However, besides the ready identification of hexamethylditin, the presence of significant amounts of 1-chloroadamantane, 1-adamantanol, and 7-methylidenebicyclo[3.3.1]nonan-3-one (7) were indicated in the mix-


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8

tures by their telltale chemical shifts.[8,9] Their identities were confirmed by comparison of VPC retention times with those of authentic samples available from another study.[8] A particularly pertinent fact was that the material balance of the reaction products based on monostannylation was extremely low (2 molar equiv of Me_3SnLi led to complete consumption of the bromo iodide and diiodide) and that no tin substitution products could be unambiguously identified in the mixtures. On the basis of these various observations, we surmised that the formation of 1,3-dehydroadamantane (8, tetrahydro[3.3.1.$1^{3,7}$.$0^{1,3}$]-decane) was strongly implicated. This propellane is known to be inert to the action of strong bases and nucleophiles (e.g. alkyllithium reagents) but reacts avidly with radicals and electrophiles.[10-13] In particular, it reacts rapidly with oxygen and water to yield a polymeric peroxide[10b] and 1-adamantanol,[11] respectively. Thus, we believe back-diffusion of O_2 into the reaction vessel while standing overnight and subsequent reaction with 8 explains, in part, the apparent complexity of the reaction mixtures obtained from the stannylation of the bromo iodide and diiodide. Although we are unable to state dogmatically the origin of 7, it is possible that this byproduct is derived from fragmentation of the polymeric peroxide under the reaction conditions.

Subsequent to the results summarized above, we prepared a sample of 8 which, on treatment with a saturated aqueous ammonium chloride solution, gave a mixture of 1-adamantanol and 1-chloroadamantane (3:1, respectively). We also treated a sample of 8 with 1 M D_2SO_4/D_2O under N_2 and, after standard workup, isolated 3-deuterio-1-adamantanol (3, X = D, Y = OH) as the only product. This latter experiment confirms unequivocally that protonation of 8 under acidic conditions yields the well-known 1-adamantyl cation which is scavenged by available nucleophiles to form the appropriate products. In contrast to [2.2.1]propellane,[14] which appears to react rapidly with Me_3SnLi,[3] 8 proved unreactive with respect to the Me_3SnM reagents (M = Li or Na). However, in connection with our NMR analyses of the product mixtures obtained from the bromoiodo and diiodo compounds (see later) we inadvertently discovered that a $CDCl_3$ solution of 8 and hexamethylditin leads to the formation of 1-chloro-3-

(6) (a) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley and Sons: New York, 1976. (c) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1.

(7) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833.

(8) Adcock, W.; Kok, G. B. *J. Org. Chem.* **1987**, *52*, 356.

(9) Krishnamurthy, V. V.; Iyer, P. S.; Olah, G. A. *J. Org. Chem.* **1983**, *48*, 3373.

(10) (a) Torupka, E. J.; Pincock, R., E. *J. Am. Chem. Soc.* **1969**, *91*, 4593. (b) Pincock, R. E.; Schmidt, J.; Scott, W. B.; Torupka, E. J. *Can. J. Chem.* **1972**, *50*, 3958.

(11) Bielmann, V. R.; Grob, C. A.; Schaub, B. *Helv. Chim. Acta* **1982**, *65*, 1728.

(12) Kogay, B. E.; Sokolenko, W. A. *Tetrahedron Lett.* **1983**, *24*, 613.

(13) (a) There are other examples of propellanes which are inert to nucleophiles but are highly reactive toward free radicals and electrophiles.[13b,c] (b) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379 and references cited therein. (c) Majerski, Z.; Zuanic, M. *J. Am. Chem. Soc.* **1987**, *109*, 3497.

(14) Wiberg, K. B.; Michl, J.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 2056.

Scheme II

$$Me_3SnSnMe_3 \xrightarrow{h\upsilon} 2\ Me_3Sn^{\cdot} \quad (1)$$

$$Me_3Sn^{\cdot} + CDCl_3 \longrightarrow Me_3SnCl + CDCl_2^{\cdot} \quad (2)$$

$$8 + Me_3SnCl \longrightarrow 3\ (X{=}Cl,\ Y{=}SnMe_3) \quad (3)$$

(trimethylstannyl)adamantane (**3**, X = Cl, Y = $SnMe_3$) on exposure to light. This result provides a plausible explanation for the puzzling appearance of the chloro tin derivative in the mixtures obtained from the stannylation of the dibromo compound after ^{13}C NMR analysis. A mechanistic pathway for the formation of the chloro tin compound is shown in Scheme II. The latter step (3) is probably ionic in nature involving the intermediate formation of the 3-(trimethylstannyl)adamant-1-yl cation. This is confirmed by the preparation of the chloro-, bromo-, and iodotin derivatives **3** (X = halogen, Y = $SnMe_3$) by treating **8** in the dark with the appropriate trimethyltin halide (see Experimental Section). Interestingly, a sample of 1-bromo-3-(trimethylstannyl)adamantane (**3**, X = $SnMe_3$, Y = Br) on prolonged storage was found to decompose slowly to yield predominantly 1-bromoadamantane. Presumably the presence of atmospheric moisture led to the formation of the 3-(trimethylstannyl)-adamant-1-yl cation which, in the absence of an abundant nucleophilic trapping species, underwent destannylation to give **8**. The latter propellane reacts rapidly with HBr to yield 1-bromoadamantane.

In light of the aforementioned results we decided to modify our *modus operandi* (see Experimental Section) in order to preclude complications associated with the sensitivity of **8** toward O_2 and electrophiles. In addition, we wished to avoid likely problems associated with LiCl being present in the reaction mixtures. Consequently, the tin reagents (Me_3SnM, M = Li or Na) were prepared by treating $Me_3SnSnMe_3$ with Li or Na in THF. The THF solutions of the reagents (2 molar equiv) were than added dropwise to a THF solution of **3** (with or without a trapping agent) maintained at 0 °C under N_2. After the reaction mixture was allowed to warm to room temperature and then to stir for a further 30 min, a sample was taken for direct analysis by vapor-phase chromatography (VPC; capillary column) before the reaction was quenched with a saturated aqueous ammonium chloride solution under N_2. A standard workup followed after ca. 12 h. The product mixtures were fully characterized by ^{13}C and ^{119}Sn NMR and VPC. All the analyses were facilitated by the availability of authentic samples of **8**, adamantane, 1-adamantanol, 1-halo(X)adamantanes (X = F, Cl, Br, and I), 1-(trimethylstannyl)adamantane, 1-halo(X)-3-(trimethylstannyl)adamantanes (**3**, X = F, Cl, Br, and I, Y = $SnMe_3$), and 1,3-bis(trimethylstannyl)adamantane (**3**, X = Y = $SnMe_3$). Only the product distribution results determined by VPC analyses of the reaction mixtures before quenching are listed in Table I. Hexamethyldistannane, which is not listed, was identified as a major reaction product in all instances except for the reactions of the chlorobromo compound (**3**, X = Cl, Y = Br) in the absence and presence of TBA (entries 1, 2, 4, and 6). For the latter reactions, it was only a minor component. This is a pertinent point which we shall refer to later.

An examination of the results (Table I) reveals several noteworthy features. Firstly, it can be seen that the product mixtures obtained from the chlorobromo, chloroiodo, and dibromo compounds on treatment with Me_3SnLi (entries 1 (and 2), 8, and 15 (and 16), respectively) are essentially unaffected when the reactions are carried out in the presence of TBA (entries 4, 10, and 18, respectively). However, the product mixtures are profoundly perturbed when the reactions are performed in the presence of DCPH (entries, 5, 11, and 19, respectively). In particular, note that the halotin and ditin substitution products are either completely or almost completely quenched in the presence of the latter trapping agent. Thus, a free radical intermediate rather than a carbanion is strongly implicated as the mediating species in the formation of the tin substitution products. A scrutiny of the corresponding results for the reactions of the same compounds with Me_3SnNa (entries 6, 12, and 20 versus entries 7, 14, and 22, respectively) corroborates this conclusion. We believe the mechanistic pathway outlined in Scheme III allows a ready rationalization of these observations. This radical chain mechanism ($S_{RN}1$ like)[15] has been previously proposed[2] to account for the results of trimethylstannylation of a series of **1**. The key feature of the mechanism is the formation and subsequent fate of the halotin radical anion ($[XC_{10}H_{14}SnMe_3]^{\cdot-}$). It can be seen that this species decomposes by two competitive pathways (bimolecular intermolecular electron transfer ($k_e[XC_{10}H_{14}Y]$) versus unimolecular fragmentation induced by intramolecular electron transfer (k_f)) whose relative rates, together with the relative rate of halogen atom abstraction ($k_a[XC_{10}H_{14}Y]$), determine the overall course of the reaction. From this study, the fact that the chlorotin compound (**3**; X = Cl, Y = $SnMe_3$) is relatively inert toward Me_3SnM reagents (M = Li or Na) and, therefore, is not an intermediate in the formation of the ditin compound in the case of the chlorobromo and chloroiodo compounds constitutes further powerful evidence for the chain nature of the radical mechanism (Scheme III). Furthermore, given that it is well established that a C–I bond is much more fragile than a C–Cl bond with respect to dissociative electron transfer,[16] the presence of more of the iodotin compound than the chlorotin derivative in the product mixture for the chloro iodide (entry 8) is perplexing in terms of a nonchain radical process[7] but clearly intelligible in terms of the pathway outlined in Scheme III.[17] It is of interest to note that a comparison of the product mixtures of the chlorobromo and chloroiodo derivatives of **1**[2] and **3** indicates that fragmentation (k_f) of the halotin radical anion is much more important than its destruction by intermolecular electron transfer (k_e) for the adamantane derivatives than the corresponding bicyclo[2.2.2]octanes. However, fragmentation is precluded for both systems when X = F. Treatment of both the fluoro bromide and fluoro iodide of **3** with Me_3SnLi or Me_3SnNa leads to the formation of only the fluorotin derivative and a minor amount of 1-fluoroadamantane (1-FAdH) (Fluoro bromide (Me_3SnLi or Me_3SnNa): fluorotin, 97 or 94%; 1-FAdH, 3 or 6%, respectively. Fluoro iodide (Me_3SnLi or Me_3SnNa): fluorotin, 92 or 88%; 1-FAdH, 8 or 12%, respectively.).

(15) Rossi, R. A.; Pierini, A. B.; Palacios, S. M. *Adv. Free Radical Chem.* **1990**, *1*, 193 and references cited therein.

(16) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1 and references cited therein.

(17) (a) The halogen atom abstraction step (k_a) of Scheme III is competitive when X or Y of **3** is I but not Cl or Br. Such reactions occur readily for alkyl iodides. In contrast, halogen atom transfer is much slower for alkyl bromides and chlorides ($(CH_3)_3CX$: X = I, $k \approx 3 \times 10^6$ M^{-1} s^{-1}; X = Br, $k \approx 4.6 \times 10^3$ M^{-1} s^{-1}; X = Cl, $k \approx 6 \times 10^2$ M^{-1} s^{-1}).[17b] (b) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195.

Table I. Product Distribution Analysis of the Reaction between 1,3-Dihaloadamantanes 3 and (Trimethylstannyl)alkali (Me_3SnM, M = Li or Na) in THF[a]

entry	compound	alkali metal (M)	addition[c]	product distribution proportions, %[b] Ad[d]	HAdH[e]	ClAdH	BrAdH	IAdH	Me_3Sn-AdH	Me_3Sn-AdCl	Me_3Sn-AdBr	Me_3Sn-AdI	Me_3Sn-AdSnMe_3	extent of reaction, %
1	3, X = Cl, Y = Br	Li	none	4	t	2			6	4	t		84	94
2	3, X = Cl, Y = Br	Li	none	t		t			7	4	t		89	95
3	3, X = Cl, Y = Br	Li	none	t	t		3		t				97	97
4	3, X = Cl, Y = Br	Li	TBA	5		2			6	5	t		82	92
5	3, X = Cl, Y = Br	Li	DCPH		t	77			23				t	100
6	3, X = Cl, Y = Br	Na	none	8			3		11	t			78	100
7	3, X = Cl, Y = Br	Na	DCPH		10	30	6		47	3			4	100
8	3, X = Cl, Y = I	Li	none	47	t	7		3	10	5		15	13	100
9	3, X = Cl, Y = I	Li	none	30		4		t	16	t			50	100
10	3, X = Cl, Y = I	Li	TBA	41	t	9		5	12	5		13	15	100
11	3, X = Cl, Y = I	Li	DCPH	t	t	76		5	14				5	100
12	3, X = Cl, Y = I	Na	none	32	2	7		3	10	5		t	41	100
13	3, X = Cl, Y = I	Na	none	43	2	14		t	19	2		8	12	100
14	3, X = Cl, Y = I	Na	DCPH	16	8	46			17	4			9	100
15	3, X = Br, Y = Br	Li	none	53			3		7		5		32	95
16	3, X = Br, Y = Br	Li	none	52			2		5		t		41	95
17	3, X = Br, Y = Br	Li	none	6	t		5		6				83	100
18	3, X = Br, Y = Br	Li	TBA	55			5		8		2		30	100
19	3, X = Br, Y = Br	Li	DCPH		17		65		18				t	100
20	3, X = Br, Y = Br	Na	none	28					7		t		65	100
21	3, X = Br, Y = Br	Na	none	t	t		t		37		t		63	100
22	3, X = Br Y = Br	Na	DCPH		21		41		38				t	100
23	3, X = Br, Y = I	Li	none	74	3		9	10					4	98
24	3, X = Br, Y = I	Li	none	97	t		3	t	t				t	100
25	3, X = Br, Y = I	Li	TBA	76	4		8	9	t				3	99
26	3, X = Br Y = I	Li	DCPH	56	9		26	9						100
27	3, X = Br, Y = I	Na	none	100										100
28	3, X = Br, Y = I	Na	none	72	8		8	8	4					100
29	3, X = Br, Y = I	Na	DCPH	83	11		6							100
30	3, X = I, Y = I	Li	none	82	t			18	t				t	100
31	3, X = I, Y = I	Li	none	71	11			18	t					95
32	3, X = I, Y = I	Li	none	63	19			4	14				t	100
33	3, X = I, Y = I	Li	TBA	93				7	t					95
34	3, X = I, Y = I	Li	DCPH	48	46			6						100
35	3, X = I, Y = I	Na	none	100										100
36	3, X = I, Y = I	Na	none	87	4			5	4					100
37	3, X = I, Y = I	Na	DCPH	78	22									100

[a] The Me_3SnM reagent (2 molar equiv) in THF (5 mL) was added to a THF solution (10 mL) of the 1,3-dihaloadamantane (3) in all cases except for entries 3, 9, 17, 24, and 32. The latter are the results of inverse addition (4 molar equiv of Me_3SnLi). All reactions were performed at the same concentration level (see Experimental Section) except for entries 13, 21, 28, and 36 which are the results for dilute solutions (5 × 1 the standard volume of THF (10 mL) was employed). [b] The VPC product proportions (%) were determined by comparison of electronically integrated peak areas, giving errors of about 2–3%. Peak areas were not corrected for appropriate response factors; therefore, the results must be viewed as being semiquantitative rather than quantitative. t ≡ trace. [c] TBA ≡ *tert*-butylamine (10 molar equiv); DCPH ≡ dicyclohexylphosphine (10 molar equiv). [d] Ad ≡ 1,3-dehydroadamantane (propellane 8). [e] HAdH ≡ adamantane.

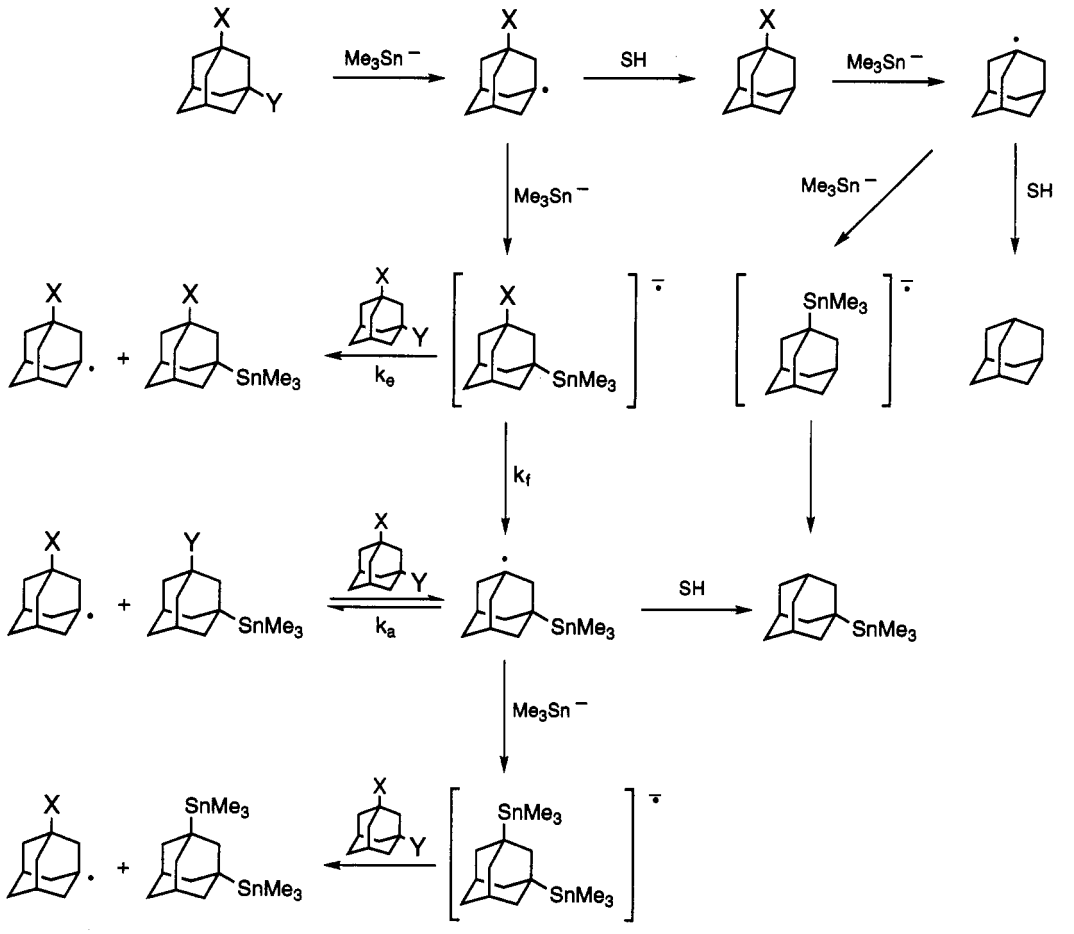
Trapping experiments on these reactions indicate that while tin substitution versus reduction is unperturbed in the presence of TBA, the presence of DCPH diverts the reaction significantly from substitution to reduction (Fluoro bromide (Me_3SnLi or Me_3SnNa): fluorotin, 58 or 27%; 1-FAdH, 42 or 73%, respectively. Fluoro iodide (Me_3SnLi): fluorotin, 7%; 1-FAdH, 93%). Finally, it is significant to note that the reaction mixtures for the fluorobromo and fluoroiodo compounds in the absence of DCPH contain only minor amounts of hexamethylditin. This is a characteristic feature of all trimethylstannylations which proceed exclusively via the mechanism outlined in Scheme III. The chloro bromide (see above) is the only other dihalo derivative of 3 which exhibits this diagnostic trait of a pure free radical chain pathway for tin substitution. For all the other dihalo derivatives of 3, hexamethylditin is a major byproduct of the reaction. Hence, other significant competing reaction pathways are apparently in operation for these compounds (see below).

Secondly, it can be seen that besides tin substitution products propellane (8) is a major constituent of the product mixtures of the chloroiodo and dibromo compounds (entries 8, 12, 15 (and 16), and 20). However, it is only a very minor component of the mixtures of the chloro bromide (entries 1 (and 2) and 6). Furthermore, whereas its presence is largely unaffected by the presence of TBA (entries 4, 10, and 18), it is either completely or almost completely quenched in the presence of DCPH. Taken at face value, the trapping experiments implicate the 3-chloro- and 3-bromoadamant-1-yl radicals as intermediates in the formation of 8. There are two possible mechanisms for the formation of 8 from these radicals. (i) Intramolecular homolytic displacement (S_H2) of halogen (Cl or Br) from the 3-halo(X)adamant-1-yl radical (X = Cl or Br). Because there is some procedence in the literature to suggest that this might be feasible,[18] we generated the 3-bromoadamant-1-yl radical by two different methods (see Experimental Section) to examine the situation. However, we found no evidence for it to be able to decompose to give propellane (8). (ii) Reduction of the 3-halo(X)adamant-1-yl radical by single electron transfer from Me_3Sn (or $Me_3Sn^{\bullet}$)[19] to form a carbanion which undergoes an intramolecular displacement (S_N2 or dissociative electron transfer) of the halogen to form 8 at a rate much faster than capture by TBA. However, a

(18) (a) Drury, R. F.; Kaplan, L. *J. Am. Chem. Soc.* **1973**, *95*, 2217. (b) Kaszynski, P.; McMurdie, N. D.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307.

(19) (a) Eberson, L. *Acta Chem. Scand.* **1984**, *B38*, 439. (b) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin-Heidelberg, 1987; Reactivity and Structure, Vol. 25.

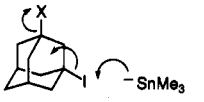
Scheme III[a]



[a] X = F, Cl, Br, or I; Y = Br or I.

serious deficiency of this latter possibility is that it is unable to account for the significant difference in propellane formation between the chlorobromo and chloroiodo compounds. The trapping experiments with DCPH (entries 5, 7, 11, and 14) clearly show that both these compounds undergo ready dissociative electron transfer on treatment with Me_3SnM (M = Li or Na) to yield the same initiating free radical species, namely, the 3-chloroadamant-1-yl radical. Thus, there is a dilemma in providing a coherent explanation for the formation of 8 based on the results of the trapping experiments (see later).

Thirdly, it can be seen that trimethylstannylation of the bromoiodo and diiodo compounds (entries 23, 27, 30, 31, and 35) gives very little or no significant tin substitution products. Propellane (8) in all instances is the predominant product of the reactions. This surprising outcome coupled with the results of the trapping experiments with DCPH (entries 26, 29, 34, and 37) strongly suggests that dissociative electron transfer between the Me_3SnM reagents and these particular dihalides (3, X = Br, Y = I and X = Y = I) does not lead to the formation of free 3-bromo- and 3-iodoadamant-1-yl radicals. The results of inverse addition (entries 3, 9, 17, 24, and 32) corroborate this conclusion as can be seen from the predominance of the ditin substitution product for the chlorobromo, chloroiodo, and dibromo derivatives but only trace amounts for the bromoiodo and diiodo compounds. The likelihood of a free carbanion as a precursor to 8 is precluded by the results of the reaction with TBA present (entries 25 and 33). Four possible mechanisms maybe envisaged for the formation of 8 from the bromoiodo and diiodo compounds. They are as follows. (i) A concerted process involving direct nucleophilic attack by Me_3Sn^- on iodine with synchronous cyclization and cleavage of the carbon–halogen bonds (see structure 9). (ii) Single electron transfer (SET) from



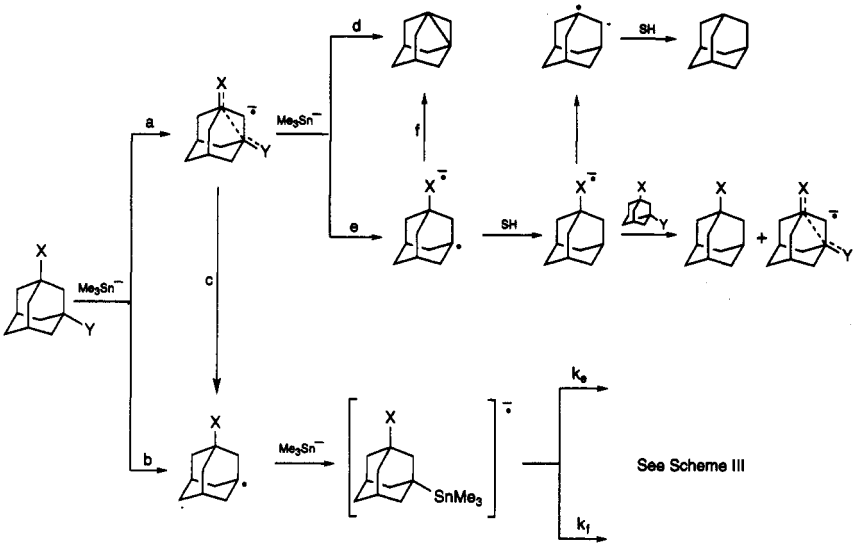
9 (X=Br or I)

Me_3Sn^- to the dihalide to yield an in-cage carbanion (see Scheme I; carbanion-like transition state, **a** ≫ **b**) which collapses rapidly to the propellane by an intramolecular displacement reaction (S_N2 or dissociative electron transfer). (iii) SET to form a radical anion adduct[20] (see Scheme I; radical-like transition state, **b** ≫ **a**) followed by a second electron transfer from Me_3Sn^- (or $MeSn^{\bullet}$)[19] before the initially formed species dissociates. The in-cage carbanion formed then decomposes rapidly as described in (ii). (iv) SET to form an intermediate delocalized radical anion (Scheme IV, step a) followed by a second electron transfer from Me_3Sn^- (Scheme IV, step a) to form propellane (8) directly without the intervention of a trappable radical or carbanion species.

Although there is no precedence in the literature for the formation of radical anions as discrete species from relatively simple haloalkanes by associative electron

(20) (a) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223 and references cited therein. (b) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098 and references cited therein.

Scheme IV[a]



[a] X = F, Cl, Br, I; Y = Br or I.

transfer,[16,20-22] we favor the latter mechanistic proposal (iv) for the following reasons. Firstly, it has the attraction of providing a unifying mechanism which also allows the puzzling formation of propellane (8) from the chlorobromo, dibromo, and chloroiodo compounds (see above) to be explained.[23] Thus, it can be seen (Scheme IV) that the delocalized radical anion can be envisaged to dissociate to yield a 3-halo(X)adamant-1-yl radical (step c) as well as to undergo a competitive dissociative electron transfer to form a diradical anion species (step e). The former radical is a key intermediate for tin substitution via the $S_{RN}1$-like route (Scheme III) while the latter species can collapse to yield propellane (8) (step f). Therefore, in the presence of an efficient radical trap such as DCPH, the stannylation of the chlorobromo, dibromo, and chloroiodo compounds can be diverted from substitution and propellane formation to yield mainly reduction products. This predicted outcome is in accord with the aforementioned experimental observations. An important feature of the mechanistic proposal (Scheme IV) is that the delocalized radical anion mediates both unimolecular and bimolecular pathways. Consequently, we were prompted to effect the stannylation reaction under conditions of high dilution to see if tin substitution versus propellane formation is significantly perturbed. The overall results are not completely compelling (see entries 13, 21, 28, and 36 in Table I) but it is pertinent that the dibromo derivative gives only substitution products under conditions of high dilution. This latter result is in line with the aforementioned competitive situation. Secondly, it can be seen (Table II) that the substituent effects for Cl, Br, and I, but not F, on the half-wave reduction potentials for the 3-halo(X)adamant-1-yl iodides (3, Y = I)[24] are large compared to the corresponding effects in the bicyclo[2.2.2]octane[25] and bicyclo[2.2.1]heptane[26] ring systems (1, Y = I and 2, Y = I, respectively). Given that polar field effects (characterized by σ_F (or σ_I) parameters) for the halogens are virtually identical[27] and, moreover, that orientational considerations suggest that polar field effects in 1, 2, and 3 (Y = I) should not be significantly different, we believe the unexpectedly large effects in 3 (Y = I) for X = Cl, Br, and I may be manifestations of very strong 1,3-"through-space" intrabridgehead interactions between the antibonding-bond MOs (σ_{CX}^*-σ_{CI}^*) in the adamantane ring system for these substituents (X = Cl, Br, and I). These interactions lead to low-lying delocalized LUMOs for these systems which facilitate the formation of relatively stable radical anions as discrete intermediates by electron transfer from Me_3Sn^-.

Table II. Polarographic Reduction Potentials ($E_{1/2}$, V) in DMF of Halo-Substituted Derivatives of 1 (Y = I), 2 (Y = I), and 3 (Y = I)

	$E_{1/2}$ (V) vs SCE[a,b]		
substituent, X	1[c]	2[d]	3[e]
H	−2.23 (0.00)	−2.31 (0.00)	−1.98 (0.00)
F	−2.13 (0.10)	−2.22 (0.09)	−1.86 (0.12)
Cl	−2.10 (0.13)	−2.15 (0.16)	−1.48 (0.50)
Br	−2.00 (0.23)	−2.10 (0.21)	−1.44 (0.54)
I	−1.95 (0.28)	−1.92 (0.39)	−1.35 (0.63)

[a] n-Bu_4ClO_4. Accurate to ±0.01V. [b] Values in parentheses are substituent effects relative to the parent compound (X = H). [c] See ref 25. [d] See ref 26. [e] See ref 24.

Conclusion

This study has revealed that substitution by Me_3Sn^- at the bridgehead of some 1,3-dihaloadamantanes 3 (X = Y = halogens) occurs exclusively by an $S_{RN}1$-type mechanism as previously proposed for 1,4-dihalobicyclo[2.2.2]octanes

(21) (a) Andrieux, C. P.; Gorande, A. L.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892 and references cited therein. (b) Lexa, D.; Savéant, J.-M.; Schäfer, H. J.; Su, K.-B.; Vering, B.; Wang, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 6162.

(22) Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193 and references cited therein.

(23) A referee raised the possibility of dicyclohexylphosphine (DCPH) adding efficiently to propellane 8 to form 1-adamantyldicyclohexylphosphine. Trapping of 8 in this fashion could explain its absence in the product mixtures obtained from the chloroiodo and dibromo compounds in the presence of DCPH. Our analyses provided no evidence for such a reaction under the conditions of stannylation. However, we did not specifically treat 8 with DCPH in order to completely preclude this possibility.

(24) Stemple, J. Z.; Vincent, M. L.; Peters, D. G.; Adcock, W. Unpublished work.

(25) Adcock, W.; Kok, G. B.; Iyer, V. S.; Peters, D. G.; Lundy, K. M.; Kitching, W. *J. Org. Chem.* **1986**, *51*, 564.

(26) Stemple, J. Z.; Vincent, M. L.; Peters, D. G.; Gangodawila, H.; Adcock, W. Unpublished work.

(27) Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 2957.

1.[2] Hence, the situation contrasts with that for 1,4-dihalobicyclo[2.2.1]heptanes 2 which, in the main, react predominantly by a polar mechanism involving the formation of a carbanion and, subsequently, [2.2.1]-propellane as a reactive intermediate.[3] However, propellane (8) formation is important for several derivatives of 3 (X = Cl, Y = I; X = Y = Br; X = Br, Y = I; X = Y = I) but it appears not to be the result of a free carbanion mediated process. This has led us to speculate on the possible formation of delocalized radical anions as discrete intermediates which is unprecedented for simple haloalkanes. A detailed electrochemical study of 1,3-dihaloadamantanes 3 (X = Y = halogens) has been initiated in an attempt to examine the veracity of this speculative proposal.[28]

Experimental Section

General. Melting and boiling points are uncorrected. Analytical vapor-phase chromatographic (VPC) analyses were performed on a Perkin Elmer 8410 gas chromatograph using a 15-m capillary column (RSL-300, 0.53-mm column). Mass spectra were recorded on a Kratos MS25RF spectrometer. The broad-band proton-decoupled ^{13}C NMR spectra were recorded at 22.53 and 75.46 MHz in the pulse Fourier transform mode on a JEOL FX-90Q and a Varian Gemini-300 spectrometer, respectively. The former instrument was used to record the ^{119}Sn NMR spectra at 33.34 MHz. Routine ^1H NMR spectra were measured with a Hitachi RR-1200 (60 MHz) spectrometer.

Tetrahydrofuran was distilled from sodium benzophenone ketyl under an atmosphere of dry nitrogen. Dicyclohexylphosphine was obtained commercially (Strem Chemicals, Inc.) and used as received. *tert*-Butylamine was dried over potassium hydroxide and distilled from calcium hydride before being stored under nitrogen over molecular sieves (4A). Hexamethylditin was prepared by a literature procedure.[7] The trimethylstannylation reactions were performed under argon in flame-dried glassware.

Compounds. Adamantane and 1-bromoadamantane were purchased from the Aldrich Chemical Co., Inc. The latter compound was also prepared by a literature procedure[29] as was 1-hydroxy-,[30] 1-fluoro-,[31] 1-chloro-,[30] and 1-iodoadamantane.[32] Literature procedures were also followed in the preparation of 1,3-dibromoadamantane,[33] 1,3-difluoroadamantane,[34] 1-fluoro-3-(trimethylstannyl)adamantane,[8] and 3-bromo-,[35] 3-chloro-,[35a] and 3-fluoroadamantane-1-carboxylic acid.[8] 7-Methylidenebicyclo[3.3.1]nonan-3-one (7) was available from another study.[8]

1-Bromo-3-chloroadamantane (3, X = Cl, Y = Br). By use of the procedure of Barton et al.,[36] dicyclohexylcarbodiimide (4.09 g, 19.8 mmol) was added to a mixture of 3-chloroadamantane-1-carboxylic acid[35a] (4.25 g, 19.8 mmol) and 1-hydroxypyridine-2(1*H*)-thione (2.52 g, 19.8 mmol) in dichloromethane (34 mL) contained in a foil-covered round-bottom flask maintained at 0 °C. After stirring for 2.25 h at 0 °C, the reaction mixture was filtered and the solvent removed in vacuo in the dark to afford the thioester. The latter compound was then dissolved in halothane ($CF_3CHBrCl$, 70 mL) and the solution was irradiated (300-W lamp) under nitrogen at reflux temperature for 40 min. The solution was then cooled before dilution with dichloromethane followed by successive washings with concentrated hydrochloric acid (3 × 15 mL), saturated aqueous sodium bicarbonate (2 × 15 mL), and water (1 × 15 mL). After drying ($MgSO_4$), the solvent was removed in vacuo to afford the crude product which, after sublimation, gave the title compound as a colorless solid (3.66 g, 74%): mp 102–103 °C (lit.[37] mp 101.5–103 °C); ^1H NMR ($CDCl_3$) δ 1.65 (2H, M), 2.13 (4H, S), 2.28 (6H, S), 2.7 (2H, S); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 62.06 (C1), 57.75 (C2), 66.63 (C3), 45.59 (C4, C10), 34.11 (C5, C1), 33.54 (C6), 47.02 (C8, C9).

A sample of the chloro bromide 3 (X = Cl, Y = Br) was also prepared by treating the acid with red mercuric oxide and bromine according to the procedure of Cristol and Firth.[38] However, the aforementioned Barton procedure proved superior.

1-Chloro-3-iodoadamantane (3, X = Cl, Y = I). The thioester of 3-chloroadamantane-1-carboxylic acid[35a] (6.63 g, 30.87 mmol) was prepared as described above for the preparation of the chloro bromide 3 X = Cl, Y = Br). A mixture of the thioester and 1,1,1-trifluoro-2-iodoethane (10.1 mL) in dry benzene (85 mL) was irradiated (300-W lamp) while the solution was kept under reflux. The solution was worked up as described above for the chloro bromide 3 (X = Cl, Y = Br) and the solvent removed in vacuo to afford the crude product. Sublimation gave the title compound as a colorless solid (7.0 g, 76%): mp 64–66 °C (lit.[37] mp 59.5–61 °C); ^1H NMR ($CDCl_3$) δ 1.75 (2 H, m), 2.17 (6H, s), 2.5 (4H, s), 2.92 (2H, s); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 66.27 (C1), 60.52 (C2), 43.69 (C3), 49.91 (C4, C10), 34.76 (C5, C7), 33.59 (C6), 45.64 (C8, C9).

An initial attempt to prepare this compound by treatment of 1-chloro-3-fluoroadamantane[8] with iodotrimethylsilane (see below) gave a mixture of the chloro iodide and diiodide which could not be separated.

1-Bromo-3-iodoadamantane (3, X = Br, Y = I). 3-Bromoadamantane-1-carboxylic acid[35] (5.7 g, 22 mmol) was converted via the thioester to the title compound in the manner outlined above for the corresponding chloro analogue (3, X = Cl, Y = I). Sublimation afforded the bromo iodide 3 (X = Br, Y = I) as a colorless solid (6.16 g, 82%): mp 81–83 °C; ^1H NMR ($DCCL_3$) δ 1.8 (2H, m), 2.13 (2H, m), 2.4 (4H, d), 2.6 (4H, d), 3.13 (2H, s); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 62.06 (C1), 61.69 (C2), 43.99 (C3), 49.86 (C4, C10), 35.76 (C5, C7), 33.57 (C6), 47.05 (C8, C9). Anal. Calcd for $C_{10}H_{14}BrI$: C, 35.22; H, 4.14. Found: C, 35.55; H, 4.32.

An initial attempt to prepare this compound by treatment of 1-bromo-3-fluoroadamantane[8] with iodotrimethylsilane (see below) gave a mixture of the bromo iodide and diiodide which could not be separated.

1,3-Diiodoadamantane (3, X = Y = I). By use of the procedure of Olah et al.,[39] a solution of 1,3-difluoroadamantane[34] (4 g, 23.22 mmol) in anhydrous dichloromethane (58 mL) was treated with iodotrimethylsilane (7.7 mL, 54.2 mmol). The reaction mixture was kept stirring in the dark at ambient temperature until the precursor fluoride was consumed (ca. 24 h; reaction continually monitored by VPC). A standard workup afforded a pale yellow solid which was chromatographed (silica gel; pentane as eluent) and sublimed to afford the title compound (8.25 g, 92%). Recrystallization from ethanol/hexane (1:1) gave the diiodide as colorless needles: mp 106–109 °C (lit.[10a] mp 110–111 °C); ^1H NMR ($CDCl_3$) δ 1.90 (4H, s), 2.63–2.70 (δH, d), 3.36 (2H, s); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 44.40 (C1, C3), 64.36 (C2), 49.97 (C4, C8, C9, C10), 36.62 (C5, C7), 33.65 (C6). Anal. Calcd for $C_{10}H_{14}I_2$: C, 30.95; H, 3.64; I, 65.41. Found: C, 31.10; H, 3.69; I, 65.20.

1-Fluoro-3-iodoadamantane (3, X = F, Y = I). 3-Fluoroadamantane-1-carboxylic acid[8] (840 mg, 2% mmol) was converted to the title compound as described above for the preparation of the chloro iodide 3 (X = Cl, Y = I). The crude product was chromatographed on alumina and then sublimed to afford a white solid (820 mg, 69%): mp 46 °C (lit.[8] mp 49 °C); ^1H NMR ($CDCl_3$) δ 1.5 (2H, m), 1.9 (4H, d), 2.15 (2H, br, s), 2.4 (4H, s), 2.65 (2H, d).

(28) Collaborative venture with Professor J.-M. Savéant, Laboratoire d'Electrochimie Moléculaire de l'Université de Paris 7, Paris, Cedex 05, France.

(29) Grob, C. A.; Sawlewicz, P. *Helv. Chim. Acta.* **1988**, *71*, 1508.
(30) Stetter, H.; Schwarz, M.; Hirschhorn, A. *Chem. Ber.* **1959**, *92*, 1629.
(31) Fort, R. C.; Schleyer, P. v. R. *J. Org. Chem.* **1965**, *30*, 789.
(32) Molle, G.; Bauer, P.; Dubois, J. E. *J. Org. Chem.* **1982**, *47*, 4120.
(33) Talaty, E. R.; Caucienne, A. E., Jr.; Dupuy, A. E. *J. Chem. Soc. C* **1968**, 1902.
(34) Bhandari, K. S.; Pincock, R. E. *Synthesis* **1974**, 655.
(35) (a) Stetter, H.; Mayer, J. *Chem. Ber.* **1962**, *95*, 667. (b) Stetter, H.; Wulff, C. *Chem. Ber.* **1960**, *93*, 1366.
(36) (a) Barton, D. H. R.; Ozbalik, N.; Vacher, B. *Tetrahedron Lett.* **1988**, *44*, 7385. (b) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901. (c) Barton, D. H. R.; Zard, S. *Z. Pure Appl. Chem.* **1986**, *58*, 675.
(37) Perkins, R. R.; Pincock, R. E. *Org. Magn. Reson.* **1976**, *8*, 165.
(38) Cristol, S. J.; Firth, W. C. *J. Org. Chem.* **1961**, *26*, 280.
(39) (a) Olah, G. A.; Narang, S. C.; Field, L. D. *J. Org. Chem.* **1981**, *46*, 3727. (b) Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225.

1-Fluoro-3-bromoadamantane (3, X = F, Y = Br). By use of the procedure of Wiberg et al.,[40] a solution of the fluoro iodide 3 (X = F, Y = I; 470 mg, 1.68 mmol) in anhydrous dichloromethane (2 mL) was treated with a solution of bromine in dichloromethane (1.7 mL of 0.5 M solution). After the reaction mixture was stirred at room temperature for 30 min, a standard workup followed by sublimation gave the fluoro bromide as a white solid (316 mg, 81%): mp 125–127 °C (lit.[8] mp 136–137 °C); ^{1}H NMR ($CDCl_3$) δ 1.5 (2H, t), 1.9 (4H, m) 2.3 (8H, m).

1-(Trimethylstannyl)adamantane (3, X = $SnMe_3$, Y = H). The title compound was prepared by treating 1-bromoadamantane (1.0 g, 5 mmol) with (trimethylstannyl)lithium (9 mmol) in the standard manner.[41] After workup, the desired compound was purified by sublimation and recrystallization from hexane to afford white crystals (0.8 g, 53.5%): mp 56–57 °C (lit.[42] mp 56–57 °C); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 28.16 (C1), 42.13 (C2, 8, 9; J_{C-Sn} = 12.21 Hz), 29.13 (C3, 5, 7; J_{C-Sn} = 48.83 Hz), 37.84 (C4, 6 10; J_{C-Sn} = 6.84 Hz), −13.17 (Me_3Sn, J_{C-Sn} = 277.83 and 290.53 Hz); ^{119}Sn NMR ($CDCl_3$, relative Me_4Sn) δ −6.47.

1,3-Bis(trimethylstannyl)adamantane (3, X = Y = $SnMe_3$). A solution of 1,3-dibromoadamantane (1.0 g, 3 mmol) in tetrahydrofuran was added dropwise to excess (trimelthylstannyl)lithium (12 mmol) in tetrahydrofuram. After a standard workup, the title compound was purified by sublimation and recrystallization from hexane to afford white crystals (0.8 g, 68.4%): mp 95–97 °C; ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 29.45 (C1,3; J_{C-Sn} = 420.89 and 440.91 Hz), 46.40 (C2, J_{C-Sn} = 12.21 Hz), 42.17 (C4, 8, 9, 10; J_{C-Sn} = 6.35 and 11.47 Hz), 30.10 (C5, 7; J_{C-Sn} = 46.38 Hz), 37.88 (C6, J_{C-Sn} = 7.32 Hz), −13.09 (Me_3Sn, J_{C-Sn} = 275.87 and 288.57 Hz); ^{119}Sn NMR ($CDCl_3$, relative to Me_4Sn) δ −7.60. Anal. Calcd for $C_{16}H_{32}Sn_2$: C, 41.55; H, 6.93. Found: C, 41.77; H, 7.07.

1,3-Dehydroadamantane or Tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane (8). By use of the procedure of Grob et al.,[11] a solution of 1,3-dibromoadamantane (2.0 g, 6.8 mmol) in anhydrous ether (12 mL) was added dropwise over a period of 1 h to lithium metal (0.11 g, 15.87 m mol) in refluxing ether (7 mL) under argon. The mixture was left under reflux with stirring for 17 h before being cooled to room temperature. The ethereal solution was the transferred by cannula into a Schlenk flask and the solvent then removed in vacuo. A sublimation probe (ethanol/liquid nitrogen cooling) was then inserted into the flask and the crude product was then carefully sublimed (25 °C/0.5 mm) to yield the propellane 8 as a white solid (610 mg, 67%), which was stored in a sealed tube under nitrogen: ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 41.5 (C1, 3), 37.27 (C2), 45.67 (C4, 8, 9, 10), 54.17 (C5, 7), 49.2 (C6). C2 and C6 may be transposed.

A sample of the propellane in tetrahydrofuran was quenched under nitrogen with a saturated aqueous ammonium chloride solution. A mixture (3:1 by VPC) of 1-adamantanol and 1-chloroadamantane, respectively, was isolated. An additional quenching experiment of the propellane in tetrahydrofuran under nitrogen with 1 M D_2SO_4/D_2O followed by a standard workup led to the isolation of 3-deuterio-1-adamantanol: ^{13}C NMR ($CDCl_3$, relative to Me_3Si) δ 68.20, 45.17 (45.06), 35.98 (35.87), 30.61 (30.10); exact mass spectrum calcd for $C_{10}H_{15}DO$ 153.1264, found 153.1222.

1-Chloro-3-(trimethylstannyl)adamantane (3, X = Cl, Y = $SnMe_3$). A solution of trimethyltin chloride (385 mg, 1.94 mmol) in anhydrous ether (1 mL) was added dropwise over a period of 1 h to a refluxing solution of 1,3-dehydroadamantane (260 mg, 1.94 mmol) in ether (3.5 mL). The reaction mixture was kept under reflux until all the trimethyltin chloride was consumed (ca. 7 days; reaction continually monitored by VPC). Removal of the solvent in vacuo followed by Kugelrohr distillation gave a colorless oil (380 mg, 58.8%) which solidified: mp 41–42 °C; ^{1}H NMR ($CDCl_3$) δ 0.00 (9H, $SnMe_3$; J_{Sn-H} = 48.48 and 50.7 Hz), 1.6–1.9 (6H, m), 1.95–2.4 (8H, m); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 70.26 (C1, J_{C-Sn} = 66.2 Hz), 51.84 (C2, J_{C-Sn} = 6.83 Hz), 31.19 (C3, J_{C-Sn} = 405.6 and 423.9 Hz), 39.83 (C4, 10; J_{C-Sn} = 10.74 Hz), 33.08 (C5, 7; J_{C-Sn} = 52.07 Hz), 35.71 (C6), 47.84 (C8, C9; J_{C-Sn} = 6.34 Hz); −12.79 ($SnMe_3$; J_{C-Sn} = 290.15 and 303.67 Hz); ^{119}Sn NMR ($CDCl_3$, relative to Me_4Sn) δ 1.97; exact mass spectrum calcd for $C_{13}H_{23}ClSn$ 332.0506, 334.0510, found 332.0902, 334.0869, calcd for ($M^{\cdot+}$ − Cl) 297.0816, 299.0822, found 297.1250, 299.1245.

1-Bromo-3-(trimethylstannyl)adamantane (3, X = Br, Y = $SnMe_3$). By use of the procedure of Grob et al.,[43] a solution of 1,3-dibromoadamantane[33] (3.5 g, 11 mol) in anhydrous ether (20 mL) was added dropwise to a stirred suspension of lithium metal (0.283 g, 20 mmol) in refluxing ether (12 mL) under argon. The mixture was left under reflux with stirring for 18 h before a solution of trimethyltin chloride (2.37 g, 11 mmol) in ether (6 mL) was added dropwise over a period of 1 h. The reaction mixture was then kept under reflux for a further 12 h. Removal of the solvent in vacuo followed by Kugelrohr distillation and recrystallization from pentane gave the title compound as a colorless solid: mp 34–37 °C (lit.[43] mp 34–35 °C); ^{13}C NMR ($CDCl_3$ relative to Me_4Si) δ 69.34 (C1, J_{C-Sn} = 67.38 Hz), 53.34 (C2), 32.76 (C3), 39.76 (C4, 10; J_{C-Sn} = 10.3 Hz), 34.23 (C5, 7; J_{C-Sn} = 51.4 Hz), 35.66 (C6), 49.45 (C8, 9), −12.76 ($SnMe_3$; J_{C-Sn} = 290.75 and 304.1 Hz); ^{119}Sn NMR ($CDCl_3$, relative to Me_4Sn) δ 1.35; exact mass spectrum calcd for $C_{13}H_{23}BrSn$ 377.9982, 379.9986, found 377.9728, 379.9641, found 299.0122 calcd for ($M^{\cdot+}$ − Br) 299.0823.

1-Iodo-3-(trimethylstannyl)adamantane (3, X = I, Y = $SnMe_3$). The title compound was prepared by modification of the Grob et al.[43] procedure described above for the preparation of the bromo tin compound 3 (X = Br, Y = $SnMe_3$) by replacing 1,3-dibromoadamantane with the diiodo analogue (3, X = Y = I; 1.26 g, 3.25 mmol). Kugelrohr distillation (145 °C/0.25 mm) followed by recrystallization from pentane gave the iodo tin compound 3 (X = I, Y = $SnMe_3$) as a colorless solid (908 mg, 66%): mp 40–42 °C; ^{1}H NMR ($CDCl_3$) δ 0.00 (9H, $SnMe_3$; J_{Sn-H} = 48.54 and 50.7 Hz), 1.5–2.1 (8H, m) 2.55–2.85 (6H, m); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 55.36 (C1, J_{C-Sn} = 64.9 Hz), 56.48 (C2), 34.37 (C3), 39.82 (C4, 10; J_{C-Sn} = 9.8 Hz), 35.24 (C5, 7, J_{C-Sn} = 50.6 Hz), 35.67 (C6), 52.64 (C8, 9), −12.74 ($SnMe_3$; J_{C-Sn} = 290 and 303.3 Hz); ^{119}Sn NMR ($CDCl_3$, relative to Me_4Sn) δ −1.68; exact mass spectrum calcd for $C_{13}H_{23}ISn$ 423.9864, 425.9868, found 297.0652, 299.0716 ($M^{\cdot-}$ − I), calcd for ($M^{\cdot+}$ − I) 297.0816, 299.0822, found 408.9563, 410.9609 ($M^{\cdot+}$ − CH_3) calcd for ($M^{\cdot+}$ − CH_3) 408.9626, 410.9632.

Trimethylstannylation of 1-Halo- and 1,3-Dihaloadamantanes 3 (X = Y = Halogens). In a typical reaction, (trimethylstannyl)alkali (Me_3SnM, M = Li or Na; 2 molar equiv) in tetrahydrofuran (prepared by reacting hexamethylditin[7] (0.67 g, 2.08 mmol) in anhydrous tetrahydrofuran (5.1 mL) with lithium or sodium (8.32 mmol) at 0 °C under argon for 5 h[7,44]) was added dropwise to a well-stirred solution of the 1-halo- or 1,3-dihalodamantane (300 mg) in THF (10 mL) maintained at 0 °C under nitrogen. After allowing the reaction mixture to warm to room temperature and then to stir for a further 30 min, a sample was taken for direct analysis by VPC before quenching the reaction with a saturated aqueous ammonium chloride solution under N_2 with stirring. The reaction mixture was then extracted with dichloromethane. After drying ($MgSO_4$), the solvent was removed in vacuo to afford the reaction product mixture which was analyzed by VPC and NMR (^{13}C and ^{119}Sn) to determine the relative proportion of products. The results from the various methods were mutually consistent.

Trimethylstannylation in the presence of *tert*-butylamine (TBA) or dicyclohexylphosphine (DCPH) was carried out in a similar fashion to that described about except that 10 molar equiv of TBA or DCPH was added.[7]

Treatment of 1-Bromo-3-iodoadamantane (3, X = Br, Y = I) with 9-(Trimethylstannyl)-9,10-dihydroanthracene. A solution of 3 (X = Br, Y = I; 50 mg, 0.147 mmol) and 9-(trimethylstannyl)-9,10-dihydroanthracene[45] in anhydrous tetrahydrofuran (2.2 mL) was placed in a well-capped Pyrex tube under nitrogen and irradiated (350-nm lamps) for 7 days. A

(40) Wiberg, K. B.; Pratt, W. E.; Matturro, M. G. *J. Org. Chem.* **1982**, *47*, 2720.
(41) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237.
(42) Kuivila, H. G.; Cosidine, J. L.; Sarma, R. H.; Mynott, R. J. *J. Organomet. Chem.* **1976**, *111*, 179.
(43) Fischer, W.; Grob, C. A. *Helv. Chim. Acta* **1978**, *61*, 1588.
(44) Alnajjar, M. S.; Kuivila, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 416.
(45) Neumann, W. P.; Hillgartner, H.; Baines, K. M.; Dicke, R.; Vorspohl, K.; Kobs, U.; Nussbeutel, U. *Tetrahedron* **1989**, *45*, 951.

VPC analysis of the reaction mixture revealed the products to be hexamethylditin, adamantane (27%), and 1-bromoadamantane (73%). No propellane 8 or its likely artefact (iodo tin compound 3 (X = I, Y = $SnMe_3$) from the reaction of 8 with Me_3SnI was detected.

Photochemical Decomposition of 1-(((3′-Bromoadamant-1′-yl)carbonyl)oxy)-1*H*-pyridine-2-thione (3, X = Br, Y = $C(O)ONC_5H_4S$). The title thioester was prepared from 3-bromoadamantane-1-carboxylic acid (1.0 g, 3.9 mmol) in the manner described above for the preparation of the bromo iodide 3 X = Br, Y = I). A solution of the thioester in deaerated anhydrous tetrahydrofuran was irradiated (300-W lamp) until the ester was consumed (ca. 3.5 h; reaction monitored by VPC). VPC analysis of the reaction mixture indicated the presence of a dominant product (>90%) with trace amounts of 1-bromoadamantane and propellane 8 also present. ^{13}C NMR established the structure of the major product to be 1-bromo-3-(2′-pyridylthio)adamantane: ^{13}C NMR ($CDCl_3$) δ 64.52 (C1), 54.04 (C2), 51.44 (C3), 41.43 (C4), 34.39 (C5, 7), 33.33 (C6), 47.88 (C8, 9), 149.62 (C2′), 121.34 (C3′), 136.31 (C4′), 127.91 (C5′), 156.48 (C6′); exact mass spectrum calcd for $C_{15}H_{18}NSBr$ 322.0266, 324.0246, found 322.0260, 324.0275.

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