# Nucleophilic Substitution Induced by Electron Transfer at the Bridgehead of Polycyclic Alkanes: Competition between Polar and Radical Pathways

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*Received November 17, 2000*

A series of 2,5(or 1,4)-dihaloadamantanes (**4** and **5**, X = Y = halogens) and 9,10-dihalotriptycenes (**7**, X = Y = halogens) as well as two 5-halo (X) adamantan-2-ones (**6**, Y = O, X = Br and I) have been treated with $Me_3SnLi$ in THF in the absence and presence of *tert*-butylamine (TBA) and dicyclohexylphosphine (DCHP). The product distributions of these reactions have been established by $^{13}C$ and $^{119}Sn$ NMR spectroscopy, vapor-phase chromatographic analyses, and GC/MS. The former compounds (**4** and **5**) appear to react exclusively by a free-radical chain process ($S_{RN}1$ mechanism) to yield tin substitution products. By contrast, the triptycenes react predominantly by a polar mechanism initiated by the formation of a carbanion. In the case of the halo ketones (**6**, Y = O, X = Br and I), a mechanistic divergence of the reaction was unexpectedly encountered. Whereas the bromo ketone provides the substitution product (**6**, Y = O, X = $SnMe_3$) in good yield (ca. 75%), apparently by a radical pathway, the iodo ketone yields a fragmentation product (ca. 95% yield) by a polar mechanism. This mechanistic switch highlights the importance of the electronegativity of the leaving group as well as substituent-induced electron delocalization as molecular factors governing the competition between radical and polar pathways.

## Introduction

Chemical transformations initiated by the injection or removal of electrons from an organic molecule have been the subject of much attention over the last 25 years.[1] Interest has focused not only on their synthetic utility but also on the factors governing electron-transfer processes as well as the various mechanistic pathways.[2,3] Of particular interest is the connection between electron pair transfer and single electron-transfer chemistry.[4]

Our interest in electron-transfer chemistry stemmed from a serendipitous discovery. We found several years ago that trimethylstannylation (nucleophilic substitution by the trimethylstannyl anion, an excellent electron donor species) of 1-bromo-4-iodobicyclo[2.2.2]- octane (**1**; X = Br, Y = I) provided a product mixture that strongly inferred an unprecedented halogen nucleofugality (Br > I) for a halogen−metal exchange (HME) or electron-transfer (ET) initiated process.[5] This result prompted us to embark on the mechanistic definition of the trimethylstannylation reaction utilizing halo bridgehead-substituted polycyclic alkanes as probe substrates. The main focus has been on the establishment of full product profiles and, in particular, how the product distributions are perturbed when the reactions are carried out in the presence of efficient free radical and carbanion traps (dicyclohexylphosphine (DCPH) and *tert*-butylamine (TBA), respectively).[6]

To date we have reported on the mechanism of trimethylstannylation of 1,4-dihalo-bicyclo[2.2.2]octanes **1**,[7] 1,4-dihalobicyclo[2.2.1]heptanes **2**,[8] and 1,3-dihaloadamantanes **3**.[9] For the former and latter systems, tin substitution at the bridgehead occurs exclusively by a free-radical chain process ($S_{RN}1$-type mechanism, see later). By contrast, most derivatives of **2** react predominantly by a polar mechanism involving the formation of

(1) (a) Eberson, L. *Electron Transfer in Organic Chemistry*; Springer-Verlag: Heidelberg, 1987. (b) Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193 and references therein. (c) Pross, A. *Theoretical and Physical Principles of Organic Reactivity*; Wiley: New York, 1995. (d) Mattalia, J.-M.; Vacher, B.; Samat, A,; Chanon, M. *J. Am. Chem. Soc.* **1992**, *114*, 4111 and references therein. (e) Guijarro, A.; Rosenberg, D. M.; Reike, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 4155 and references therein. (f) Rossi, R. A.; Pierini, A. B.; Santiago, A.N. *Org. React.* **1999**, *54*, 1 and references therein.

(2) (a) Kornblum, N. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1982; Supplement F, Chapter 10. Norris, R. K. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1983; Supplement D, Chapter 16. Rossi, R.; Pierini, A. B.; Penenory, A. B. In *The Chemistry of Halides, Pseudohalides, and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1995; Supplement DZ, Chapter 24. (b) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983.

(3) (a) Rossi, R. A.; Pierini, A. B.; Palacios, S. M. *Adv. Free Radical Chem.* **1990**, *1*, 193 and references therein. (b) Savéant, J.-M. *Tetrahedron* **1994**, *50*, 10117 and references therein.

(4) (a) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 198. (d) Chanon, M. *Acta Chem. Scand. B* **1992**, 695. (e) Lund, H.; Daasbjerg, K.; Lund, T.; Pedersen, S. U. *Acc. Chem. Res.* **1995**, *28*, 313. (f) Speiser, B. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2471 (g) Costentin, C.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 2329. (h) Bakken, V.; Danovich, D.; Shaik, S.; Schlegel, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 130.

(5) Adcock, W.; Iyer, V. S.; Kok, G. B.; Kitching, W. *Tetrahedron Lett.* **1983**, *24*, 5901.

(6) (a) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. (b) Alnejjar, M. S.; Kuivila, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 416.

(7) Adcock, W.; Iyer, V. S.; Kitching, W.; Young, D. *J. Org. Chem.* **1985**, *50*, 3706.

(8) Adcock, W.; Gangodawila, H. *J. Org. Chem.* **1989**, *54*, 6040.

(9) Adcock, W.; Clark, C. I. *J. Org. Chem.* **1993**, *58*, 7341.

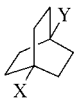
10.1021/jo001638w CCC: $20.00 
Published on Web 04/25/2001

**Scheme 1**

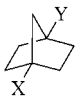
$$Me_3Sn\bullet(Y\text{-}R\text{-}X)^{\bullet-} \equiv a(Me_3Sn\bullet\bullet Y{:}^{-}R\text{-}X) \leftrightarrow b(Me_3Sn\bullet : Y^{-}\bullet R\text{-}X)$$

R = polycyclic alkyl system ; X=substituent; Y=halogen leaving group

a carbanion and, subsequently, [2.2.1]propellane as a reactive intermediate to provide the various tin substitution products. Two particularly salient features emerged from the study of **2** and **3**. First, for **2** there is a clear



**1**



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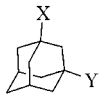
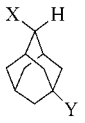


**3**

competition between the prevailing polar reaction pathway in most instances and a free-radical route that is delicately balanced.[8,10] 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. Thus, in accord with the configuration mixing model (CM) developed by Pross, Shaik, and others,[1c,4a−e] a valence bond configurational description of the transition state (TS) for trimethylstannylation of bridgehead halopolycycloalkanes can be denoted as shown in Scheme 1. The relative magnitude of the weighing factors (a and b) govern the partitioning between the two mechanisms. Thus, a carbanion mechanism is predominant when a ≫ b whereas a radical pathway dominates when b ≫ a. Second, similar to the situation for **2**, propellane (1,3-dehydroadamantane) formation is important for several derivatives of **3** (X = Cl, Y = I; X = Y = Br; X = Br, Y = I; X = Y = I), but unlike the highly reactive [2.2.1]-propellane it is not a reactive intermediate mediating the formation of tin substitution products. Unfortunately, the results of the trapping experiments for **3** were equivocal; thus, a dilemma arose in providing a coherent explanation for the formation of 1,3-dehydroadamantane.[9] This led us to speculate on the possible formation of delocalized radical anions as discrete intermediates. However, this idea was not supported by a subsequent detailed electrochemical study of the mono- and dihalo derivatives of **3**.[11] The latter study clearly implicates a very fast intramolecular $S_N$-2 type substitution of 3-halo (X) adamant-1-yl carbanions as the pathway of propellane formation. Thus, it appears that propellane formation versus tin substitution in the trimethylstannylation of **3** is simply another manifestation of competing polar and radical pathways. Most significantly, the competition between the two pathways for **3** is, like that for **2**, intelligible within the framework of the single TS model (Scheme 1) by bearing in mind that the relative magnitude of *a* and *b* is highly sensitive to the following structural factors:[8] (i) the electronegativity of the leaving groups, (ii) the s character of the exocyclic bridgehead orbital, and (iii) substituent-induced electron delocalization.

(10) Adcock, W.; Clark, C. I. *J. Org. Chem*. **1995**, *60*, 723.
(11) Adcock, W.; Clark, C. I.; Houman, A.; Krstic, A. R.; Pinson, J.; Savéant, J.-M.; Taylor, D. K.; Taylor, J. F.*J. Am. Chem. Soc.* **1994**, *116*, 4653.

In an attempt to shed further light on the molecular factors controlling the competition between polar and radical pathways in the trimethylstannylation of bridgehead-substituted halo polycyclic alkanes we have extended our studies to include 2,5 (or 1,4)-dihaloadamantanes (**4** and **5**), 5-substituted (X)-2-adamantanones (**6**, Y = O), and 9,10-dihalotriptycenes (**7**). Herein we report this sequel to our investigations.



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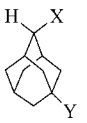

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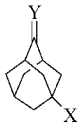

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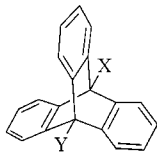


**7**

## Results and Discussion

**2,5-Dihaloadamantanes 4 and 5 (X = Y = Halogen).** Product distributions for treatment of various dihalo derivatives of **4** and **5** with $Me_3SnLi$ (1 and 2 molar equiv) in THF at 0 °C in the absence and presence of DCPH are listed in Table 1. The overall procedures such as the preparation of $Me_3SnLi$, mode of addition, reaction time, and workup were the same as described in a previous paper.[9] 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 adamantane, 1- and 2-halo (X) adamantanes (X = Cl, Br, and I), 1- and 2-(trimethylstannyl)adamantane, (*E*)- and (*Z*)-2-chloro-5-(trimethylstannyl)adamantane (**4** and **5**, X = Cl and Y = $SnMe_3$, respectively),[12] (*E*)- and (*Z*)-2-bromo-5-(trimethylstannyl)adamantane (**4** and **5**, X = Br and Y = $SnMe_3$, respectively),[12] and (*E*)- and (Z)-1,4-bis(trimethylstannyl)adamantane (**4** and **5**, X = Y = $SnMe_3$, respectively).[12] Only the product distribution results determined by VPC analyses of the reaction mixtures before quenching are listed in Table 1. Hexamethyldistannane, which is not listed, was identified as a major reaction product in all instances. It should be noted that the data for the chloro and bromo iodides (entries 7−12 and 19−24) have been presented previously in connection with another investigation.[13]

Before examination of the results (Table 1), it is instructive to note that the trimethylstannylation of 1-bromo- and 1-iodoadamantanes (1-BrAdH and 1-IAdH, respectively)[6a,9,14] and 2-bromoadamantane (2-BrAdH)[6a,14,15] has been shown to occur by free radical intermediates in an $S_{RN}1$ like reaction. Moreover, Santiago et al.[14] have established by competition experiments that 1-BrAdH is 1.4 times more reactive than 2-BrAdH toward $Me_3Sn^-$ ions. This relative reactivity parallels their observed reduction potentials determined by cyclovoltammetry[16] as expected for an electron-transfer initiated reaction. For this study, we corroborated the trimethylstannylation

(12) Adcock, W.; Lünsmann, D.; Trout, N. A. *J. Org. Chem*. **1998**, *63*, 7231.
(13) Adcock, W.; Clark, C. I.; Trout, N. A. *Tetrahedron Lett*. **1994**, *35*, 297.
(14) Santiago, A. N.; Stahl, A. E.; Rodriguez, G. L.; Rossi, R. A. *J. Org. Chem*. **1997**, *62*, 4406.
(15) Duddeck, H.; Islam, M. R. *Chem. Ber*. **1984**, *117*, 565.
(16) (a) Dubois, J.-E.; Bauer, P.; Keddani, B. *Tetrahedron Lett*. **1985**, *26*, 57. (b) Dubois, J.-E.; Bauer, P.; Briand, S. *Tetrahedron Lett*. **1988**, *29*, 3935.

**Table 1. Product Distribution Analysis of the Reaction between (*E*)- and (*Z*)-2,5-Dihaloadamantanes (4 and 5, respectively) and (Trimethylstannyl)lithium in THF**

| | | | | product distribution proportions, %[a–d] | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| entry no. | compd | equiv of $Me_3SnLi$ | additive | HAdH | 2ClAdH | 1BrAdH | 2BrAdH | 1SnAdH | 2SnAdH | *E* 2Cl5Sn | *Z* 2Cl5Sn | *E* 2Br5Sn | *Z* 2Br5Sn | *E* 2I5Sn | *Z* 2I5Sn | *E* 2Sn5Sn | *Z* 2Sn5Sn | extent of reaction, % |
| 1 | **4**; Y = Br, X = Cl | 1 | none | | 16 | | | 3 | 2 | 59 | | | | | | 10 | 10 | 72 |
| 2 | **4**; Y = Br, X = Cl | 2 | none | | 5 | 1 | | 1 | 1 | 57 | | | | | | 17 | 19 | 100 |
| 3 | **4**; Y = Br, X = Cl | 2 | DCPH | | 93 | | | | | 7 | | | | | | | | 90 |
| 4 | **5**; Y = Br, X = Cl | 1 | none | | 16 | | | | | | 76 | | | | | 4 | 4 | 46 |
| 5 | **5**; Y = Br, X = Cl | 2 | none | | 8 | 1 | | 1 | 1 | | 73 | | | | | 8 | 8 | 100 |
| 6 | **5**; Y = Br, X = Cl | 2 | DCPH | | 97 | | | | | | 3 | | | | | | | 84 |
| 7 | **4**; Y = I, X = Cl | 1 | none | | 20 | | | t | | 68 | | | | 3 | 3 | 3 | 3 | 76 |
| 8 | **4**; Y = I, X = Cl | 2 | none | | 7 | | | 1 | 1 | 72 | | | | t | t | 9 | 10 | 100 |
| 9 | **4**; Y = I, X = Cl | 2 | DCPH | t | 88 | | | | | 12 | | | | | | t | t | 100 |
| 10 | **5**; Y = I, X = Cl | 1 | none | | 55 | | | | | | 41 | | | | | 2 | 2 | 56 |
| 11 | **5**; Y = I, X = Cl | 2 | none | | 11 | | | t | 1 | | 76 | | | | | 6 | 6 | 100 |
| 12 | **5**; Y = I, X = Cl | 2 | DCPH | | 93 | | | | | | 7 | | | | | t | t | 100 |
| 13 | **4**; Y = Br, X = Br | 1 | none | | | 3 | 7 | 4 | 16 | | | 5 | | | | 29 | 36 | 46 |
| 14 | **4**; Y = Br, X = Br | 2 | none | | | t | 2 | 2 | 8 | | | 3 | | | | 39 | 46 | 84 |
| 15 | **4**; Y = Br, X = Br | 2 | DCPH | 5 | | 27 | 49 | 4 | | | | | | | | 7 | 8 | 65 |
| 16 | **5**; Y = Br, X = Br | 1 | none | | | 2 | 5 | 1 | 15 | | | | 6 | | | 31 | 40 | 57 |
| 17 | **5**; Y = Br, X = Br | 2 | none | | | 1 | 5 | 1 | 9 | | | | 4 | | | 36 | 44 | 100 |
| 18 | **5**; Y = Br, X = Br | 2 | DCPH | 15 | | 32 | 40 | | | | | | | | | t | 13 | 69 |
| 19 | **4**; Y = I, X = Br | 1 | none | | | | 22 | 4 | | | | 23 | | 12 | 14 | 13 | 13 | 66 |
| 20 | **4**; Y = I, X = Br | 2 | none | | | | 2 | 5 | 3 | | | 11 | | t | t | 38 | 40 | 100 |
| 21 | **4**; Y = I, X = Br | 2 | DCPH | 8 | | | 70 | 7 | | | | 3 | | | | 6 | 6 | 100 |
| 22 | **5**; Y = I, X = Br | 1 | none | | | | 25 | 3 | 1 | | | | 27 | 6 | 8 | 15 | 15 | 61 |
| 23 | **5**; Y = I, X = Br | 2 | none | | | | 9 | 2 | 3 | | | | 24 | 3 | 3 | 28 | 28 | 94 |
| 24 | **5**; Y = I, X = Br | 1 | DCPH | 5 | | | 80 | 5 | | | | | 2 | | | 4 | 4 | 100 |

[a] The VPC product proportions (%) were determined by comparison by electronically integrated peak areas, giving errors to about 2−3%. Peak areas were not corrected for appropriate response factors.Ratios determined by $^{13}C$ NMR corresponded well with the VPC results. [b] HAdH ≡ adamantane; Sn = $SnMe_3$. [c] DCPH = dicyclohexylphosphine (10 molar equiv). [d] t = trace.

**Scheme 2**[a–f]

$XC_mH_nY + Me_3Sn^- \longrightarrow XC_mH_n^\bullet + Y^- + Me_3Sn^\bullet$ (step 1)

$XC_mH_n^\bullet + Me_3Sn^- \longrightarrow [XC_mH_nSnMe_3]^{\bullet-}$ (step 2)

$[XC_mH_nSnMe_3]^{\bullet-} + XC_mH_nY \xrightarrow{k_t} XC_mH_nSnMe_3 + XC_mH_n^\bullet + Y^-$ (step 3)

$[XC_mH_nSnMe_3]^{\bullet-} \xrightarrow{k_f} X^- + {}^\bullet C_mH_nSnMe_3$ (step4)

$XC_mH_nY + {}^\bullet C_mH_nSnMe_3 \rightleftharpoons YC_mH_nSnMe_3 + XC_mH_n^\bullet$ (step 5)

${}^\bullet C_mH_nSnMe_3 + Me_3Sn^- \longrightarrow [Me_3SnC_mH_nSnMe_3]^{\bullet-}$ (step 6)

$[Me_3SnC_mH_nSnMe_3]^{\bullet-} + XC_mH_nY \longrightarrow Me_3SnC_mH_nSnMe_3 + XC_mH_n^\bullet + Y^-$ (step 7)

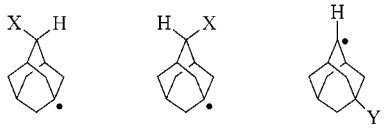
${}^\bullet C_mH_nSnMe_3 + SH \longrightarrow Me_3SnC_mH_{n+1} + S^\bullet$ (step 8)

$2Me_3Sn^\bullet \longrightarrow Me_3SnSnMe_3$ (step 9)

[a] $m = 10$, $n = 14$; X = halogen; Y = Br or I. [b] $Li^+$ is understood to be present as the counterion. [c] For expedience, the radical−halide ion adduct is understood to occur prior to steps 1, 3, and 7. [d] The tin reagent is given as being monomeric for pictorial clarity. However, it should be remembered that its state of aggregation is unknown. [e] Solvent ≡ SH. [f] An additional dissociative electron-transfer step may involve the radical anions ($[XC_mH_nSnMe_3]^{\bullet-}$ and $[Me_3SnC_mH_nSnMe_3]^{\bullet-}$) and $XC_mH_nSnMe_3$ when X = Br or I.

results of Kuivila et al.[6a] for 2-BrAdH in the presence and absence of trapping agents (DCPH and TBA). In addition, we also found that 2-IAdH behaves similarly by giving almost identical product mixtures on treatment with $Me_3SnLi$ in THF at 0 °C in the absence and presence of DCPH and TBA (substitution (%)/reduction (%): 91/9 (none), 93/7 (TBA), 5/95 DCPH)). Not suprisingly, in accord with others,[15] we found 2-ClAdH is relatively unreactive (ca. 16% reaction after 1 h; $Me_3SnLi$/THF/0 °C) toward $Me_3Sn^-$ compared to the other 2-haloadamantanes. This is to be expected for an intermolecular electron-transfer initiated reaction given that the reduction potential of alkyl chlorides is well-known to be much higher than the corresponding bromides and iodides.[11]

A scrutiny of the data in Table 1 reveals a product distribution pattern that is somewhat reminescent of that previously reported for the corresponding dihalo derivatives of **1**. The results for the latter were clearly intelligible in terms of the $S_{RN}1$-like mechanism shown in Scheme 2. The key feature of this mechanism is the formation (step 2) and subsequent fate (steps 3 and 4) of the halo tin radical anion ($[XC_mH_nSnMe_3]^{\bullet-}$). This species decomposes by two competitive pathways (bimolecular intermolecular electron transfer (step 3) and unimolecular electron transfer (step 4)) whose relative rates depend importantly inter alia on the nature of the substituent (X) and the initial nucleofuge (Y). The relative rates of steps 3 and 4 coupled with the competitiveness of the halogen atom abstraction step (step 5) determine the overall course of the reaction. There are several characteristic and distinctive features of the results listed in Table 1 which highlight that product formation from the trimethylstannylation of **4** and **5** is being mediated by the mechanism outlined in Scheme 2. First, it can be seen that the presence of DCPH, an excellent alkyl radical trap,[6] is able to divert the reactions from predominant tin substitution to mainly reduction products by trapping the initially formed radicals (**8** and **9**, X = Cl or Br). It is important to note that in the case of the dibromo compounds (**4** and **5**, X = Y = Br) the formation of significant amounts of both 1-BrAdH and 2-BrAdH indicates not only the formation of **8** and **9** (X = Br) but also **10** (Y = Br). In both cases (entries 15 and 18), 2-BrAdH is formed in slightly greater amounts than 1-BrAdH. The ratios (2-BrAdH/1-BrAdH = 1.8 and 1.3, respectively) parallel the fact that 1-BrAdH is more reactive than 2-BrAdH (see above).[14] It should be noted that 7-methylenebicyclo[3.3.1]non-2-ene[17] was not detected in the various reaction product mixtures. This five-bond heterolytic fragmentation product is a clear telltale sign of any carbanion involvement. Thus, no polar pathway appears to occur in the trimethylstannylation of **4** and **5**. This conclusion is reinforced by the observation that treatment of **4** and **5** (X = Y = Br; X = Br and Y = I) with $Me_3SnLi$ in the presence of TBA, an effective trapping agent of free carbanions,[6a,8a,10] did not lead to any significant perturbation of the product distribution. Second, the formation of the ditin compounds (**4** and **5**, X = Y = $SnMe_3$) in the case of the chloro bromides and chloro iodides (**4** and **5**; X = Cl, Y = Br and I, respectively) constitutes powerful evidence for the chain nature of the radical mechanism (Scheme 2) since the chloro tin derivatives (**4** and **5**, X = Cl and Y = $SnMe_3$), being relatively inert toward $Me_3SnLi$, are not intermediates in their formation. Thus, a competition between inter- and intramolecular electron transfer (Scheme 2, steps 3 and 4, respectively) involving an initially formed radical-anion (step 2) is implicated followed by steps 6 and 7 to form the ditin products. Interestingly, in connection with other studies,[18] we prepared the fluoro tin compounds (**4** and **5**, X = F and Y = $SnMe_3$) by treatment of the corresponding fluoro bromides (**4** and **5**, X = F and Y = Br) with excess (3 molar equiv) $Me_3SnLi$. No ditin compounds were detected in these reactions. Hence, step 4 is precluded from competing against step 3 when X = F. Finally, the aforementioned evidence for a chain rather than a nonchain radical process is reinforced by the presence of the iodo tin compounds (**4** and **5**, X = I and Y = $SnMe_3$) in the product mixtures of the chloro iodide




**8** **9** **10**

(17) Adcock, W.; Coope, J.; Shiner, V. J., Jr.; Trout, N. A. *J. Org. Chem.* **1990**, *55*, 1411 and references therein.

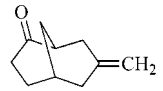
(18) (a) Adcock, W,; Trout, N. A. *J. Org. Chem.* **1991**, *56*, 3229. (b) Adcock, W.; Trout, N. A. *Magn. Reson. Chem.* **1998**, *36*, 181.

(entry 7) and, in particular, of the bromo iodides (entries 19 and 22) on treatment with just 1 molar equiv of $Me_3SnLi$. Within the framework of a nonchain radical reaction, these results infer that C−Cl and C−Br bonds can compete effectively for the acceptance of an electron against a C−I bond with respect to dissociative electron transfer. The experimental evidence from electrochemical studies[11] strongly suggests that such a scenario is not possible. However, the competitiveness of step 5 of the chain mechanism (Scheme 2) when Y = I[19] readily allows the formation of the iodo tin compounds to be explained.

A pertinent structural difference between the epimeric dihalo compounds (**4** and **5**, X = Y = halogen) is that the C−X and C−Y bonds in **4** are orientated trans-coplanar with respect to the bridging ethano bonds but not in **5**. Consequently, orbital overlap in the former structure is properly aligned to facilitate and maximize intramolecular dissociative electron transfer (step 4) compared to the latter. It is interesting, therefore, to speculate whether this stereoelectronic factor is responsible for the observed larger ratio of the combined iodo tin and ditin products to the chloro or bromo tin products for **4** (X = Cl and Y = I, X = Br and Y = I) compared to the corresponding ratios for **5** (see Table 1; entries 8, 11, 20, and 23). Another pertinent ratio in this context is the much larger ratio of ditin to chloro tin products for **4** (X = Cl and Y = Br) compared to the corresponding chloro bromide of **5** (see Table 1; entries 2 and 5). However, no definite conclusions can be drawn because of the uncertainty of the other variable, namely, the rate of intermolecular dissociative electron transfer (Scheme 2, step 3). What is clear though is that a comparison of the product mixtures of the chlorobromo and chloroiodo derivatives of **1**,[7] **3**,[9] and **4**, for which the $S_{RN}1$-like mechanism is applicable, indicates that the effectiveness of step 4 compared to step 3 is in the order **3** > **1** > **4**.

A final noteworthy feature of the results listed in Table 1 concerns the *E*/*Z* ratio of the ditin products. It can be seen that for the chloro bromides, chloro iodides, and bromo iodides the ratio is effectively unity. By contrast, the corresponding ratio for the dibromo compounds is significantly less than unity. The result for the former bunch of compounds is understandable in terms of the capture of **10** (Y = $SnMe_3$) by $Me_3Sn^-$ occurring with random stereochemistry.[12,13,20] For the dibromo derivatives, the ditin compounds are formed not only by the $Me_3Sn^-$ capture of **10** (Y = $SnMe_3$) but also **10** (Y = Br). Consequently, the *E*/*Z* ratio of less than unity demands a modest *zu* face preference (*E*/*Z* = 45/55) for the capture of the latter radical. Interestingly, this diastereoselectivity is identical to that reported for the corresponding fluoro radical (**10**, Y = F),[13] which has been ascribed to an electrostatic steering effect ($\sigma_F$ values: F, 0.40, Br, 0.44).[20]

**5-Substituted (X) Adamantan-2-ones (6, Y = O).** Because reduction potential data[11,16] were available to suggest that it should be possible to selectively induce substitution of Br or I at the bridgehead of adamantane by means of an electron-transfer-mediated reaction in the presence of a carbonyl moiety, we treated 5-bromo- and 5-iodo-2-adamantanone (**6**, X = Br and I, Y = O, respectively) with $Me_3SnLi$ with the express purpose of obtaining the corresponding tin ketone (**6**, X = $SnMe_3$, Y = O) by a more direct synthesis than that reported.[18a] We found that whereas the bromo ketone provided the desired product in reasonable yields (ca. 70%), the iodo ketone gave a mixture containing predominantly 7-methylenebicyclo[3.3.1]nonan-2-one (**11**, ca. 90%) together with a minor amount of adamantan-2-one (**6**, X = Y, Y = O; ca. 10%). Interestingly, this five-bond fragmentation



**11**

product is known to be formed efficiently on treatment of the chloro ketone (**6**, X = Cl, Y = O) with sodium−potassium alloy.[21] By analogy with other Grob-like fragmentation processes,[22,23] a carbanion species (**6**, X = Li, Y = O) is clearly implicated as the key intermediate formed on attempted stannylation of the iodo ketone (**6**, X = I, Y = O). It should be noted that the fact that 4-oxaadamantane-1-carboxylic acid (**6**, X = COOH, Y = O) can be converted in good yields (ca. 80%) to the corresponding bromo ketone (**6**, X = Br, Y = O) via a radical mediated Barton reaction without a trace of **11** precludes the 4-oxaadamant-1-yl radical as the penultimate source of the fragmentation product **11** (see conversion of **6** (X = COOH, Y = O) to **6** (X = Br, Y = O) in the Experimental Section). In an attempt to provide direct evidence for the nature of the intermediates (radical or carbanion) formed in the aforementioned stannylation reactions, we carried out appropriate trapping experiments in the presence of DCPH and TBA, respectively. The product distribution results for these experiments are listed in Table 2 together with those obtained in the absence of trapping experiments. It can be seen that in all instances the trapping agents do not effect any major perturbation of the product distributions. Hence, no definitive conclusions can be drawn from these results regarding the nature of the intermediates. However, given the ineffectiveness of TBA at trapping highly reactive 3-halo (X) adamant-1-yl carbanions presumed formed in the trimethylstannylation of **3** (X = Cl, Y = I;

(19) (a) The halogen atom abstraction reaction (Scheme 2, step 5) is only competitive when Y of **4** and **5** is I and not Br. Such reactions occur readily for alkyl iodides. In contrast, halogen atom transfer is much slower for alkyl bromides ($(CH_3)_3CX$: X = I, $k \approx 3 \times 10^6$ $M^{-1}s^{-1}$; X = Br, $k \approx 4.6 \times 10^3$ $M^{-1}s^{-1}$).[19b] Step 5 is in direct competition with the trapping of the radical by $Me_3Sn^-$ (step 6). The rates of such reactions maybe at, or close to, the diffusion limit.[3b] (b) Newcomb, M.; Sanchez, R. M. Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195.

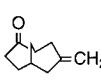
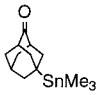
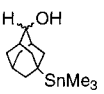
(20) Adcock, W.; Trout, N. A. *Chem. Rev.* **1999**, *99*, 1415.

(21) Hamon, D. P. G.; Taylor, G. F.; Young, R. N. *Synthesis* **1975**, 428. Hamon, D. P. G.; Young, R. N. *Aust. J. Chem.* **1976**, *29*, 145.

(22) (a) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1. Grob, C. A. *Ibid.* **1969**, *8*, 535. Grob, C. A.; Kunz, W.; Marbet, P. R. *Tetrahedron Lett.* **1975**, 2613. Grob, C. A.; Bolleter, M.; Kunz, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 708. (b) Pertinent reactions are the fragmentation of 4-halobicyclo[2.2.2]oct-1-yl iodides[22c−f] on treatment with *tert*-butyllithium and fragmentation of (*E*)-1-bromo-4-adamantyl methanesulfonate[22g] on reaction with ethylenediaminechromium(II).[22h] (c) Wiberg, K. B.; Pratt, W. E.; Matturro, M. G. *J. Org. Chem.* **1982**, *47*, 2720. (d) Adcock, W.; Iyer, V. S. *J. Org. Chem.* **1985**, *50*, 1538. (e) See footnote 4a of ref 7. (f) Babler, J. H.; Moorman, A. E.; *J. Org. Chem.* **1976**, 41, 1477. (g) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York 1978.

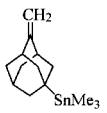
(23) (a) It is of interest to note that fragmentation predominates in the $S_{RN}1$ reactions of some 1,3-dihaloadamantanes(**3**, X = Y = I; X = Y = Br; X = Cl, Y = Br) with various carbanionic nucleophiles.[23b] However, in these reactions fragmentation is due to the formation of a carbanion from the initially formed monosubstitution product under the basic conditions. (b)Lukach, A. E.; Santiago, A.N.; Rossi, R. A. *J. Org. Chem.* **1997**, *62*, 4260.

**Table 2. Product Distribution Analysis of the Reaction between 5-Haloadamantan-2-ones (6, Y = O) and $Me_3SnLi$ in THF[a,b]**

| | | | product distribution proportions, % | | | | | |
|---|---|---|---|---|---|---|---|---|
| entry no. | compound | additive |  |  |  |  |  | extent of reaction,% |
| 1 | **6**, X=Br Y=O | none | 21 | | 4 | 75 | | 100 |
| 2 | **6**, X=Br Y=O | TBA | 17 | | 3 | 80 | | 100 |
| 3 | **6**, X=Br Y=O | DCPH | 25 | | 6 | 60 | 9 | 100 |
| 4 | **6**, X=I Y=O | none | 6 | | 94 | | | 100 |
| 5 | **6**, X=I Y=O | TBA | 9 | | 88 | 3 | | 100 |
| 6 | **6**, X=I Y=O | DCPH | 6 | 9 | 85 - | | | 100 |

[a] Product proportions (%) determined by VPC. See footnotes a−c of Table 1. Two molar equivalents of $Me_3SnLi$ was used in all reactions. [b] TBA ≡ *tert*-butylamine (10 molar equiv).

**Table 3. Product Distribution Analysis of the Reaction between 2-Methylene-5-haloadamantanes (6, Y=$CH_2$) and $Me_3SnLi$ in THF[a,b]**

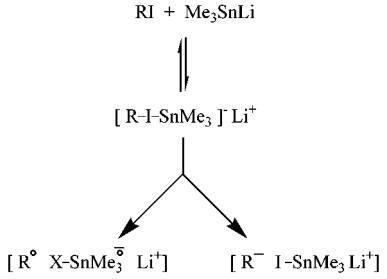
| | | |  |  | |
|---|---|---|---|---|---|
| entry no | compound | additive | | | extent of reaction,% |
| 1 | **6**, X=Br Y=$CH_2$ | none | 3 | 97 | 100 |
| 2 | **6**, X=Br Y=$CH_2$ | TBA | 5 | 95 | 100 |
| 3 | **6**, X=Br Y=$CH_2$ | DCPH | 14 | 86 | 100 |
| 4 | **6**, X=I Y=$CH_2$ | none | 17 | 83 | 100 |
| 5 | **6**, X=I Y=$CH_2$ | TBA | 9 | 91 | 100 |
| 6 | **6**, X=I Y=$CH_2$ | DCPH | 33 | 67 | 100 |

[a] Product proportions (%) determined by VPC. See footnotes a and b of Table 2. [b] TBA ≡ *tert*-butylamine (10 molar equiv).

X = Y = Br; X = Br, Y = I; X = Y = I)[9] (see the Introduction), it is not surprising that the efficacy of fragmentation of **6** (X = Li, Y = O) to **11** in the solvent cage precludes quenching. The failure of DCPH to significantly divert tin substitution to mainly reduction for the trimethylstannylation of the bromo ketone (**6**, X = Br, Y = O) was entirely unexpected. This conundrum is heightened by the product distribution results listed in Table 3 for the trimethylstannylation of the bromo- and iodoalkenes (**6**, X = Br and I, Y = $CH_2$). Here, fragmentation is precluded; thus, efficient trapping of radical or carbanions intermediates was expected based on our previous studies.[7−10] We can offer no explanation for this unusual scenario.

It is clear from the aforementioned results that since trimethylstannylation of 1-iodoadamantane (**3**, X = I, Y = H) proceeds exclusively by a free-radical process,[9] carbonyl substitution at C4 has profound consequences on the mechanism and course of the reaction. Within the framework of the single TS model (Scheme 1), the switch from a free radical to a polar mechanism (b ≫ a ⟹ a ≫ b) on going from **3** (X = I, Y = H) to **6** (X = I, Y = O) further highlights the importance of electron delocalization as a factor (see introduction) tipping the balance between competing radical and polar pathways. The contrasting situation for the trimethylstannylation of **6** (X = Br, Y = O), where tin substitution prevails (Table 2), suggests that here electron delcalization is unable to override the electronegativity effect of the leaving group (Br > I) which promotes b ≫ a (Scheme 1). Hence, the radical pathway continues to dominate.

**Scheme 3**




It is important to note, however, that a pronounced halogen effect (Br versus I) on the mechanism of lithium−halogen interchange between an organic halide and organolithium compounds is well-known.[24] Thus, in this connection, "ate complexes" have been postulated as intermediates in the lithium−iodine exchange reaction[24] and, in some cases, detected spectroscopically.[25] Further, the "ate complex" between phenyllithium and perfluoroiodobenzene has been crystallized as a stable TMEDA adduct.[26] Consequently, an alternative explanation for the mechanistic changeover on trimethylstannylation of **3** (X = I, Y = H) and **6** (X = I, Y = O) can be advanced based on the idea of bifurcation (radical and polar) from an intermediate "ate complex" (Scheme 3) rather than a TS (Scheme 1).

(24) Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *352*, 1 and references therein.
(25) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414 and references therein.
(26) Farnham, W. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2449.

**Table 4. Product Distribution Analysis of the Reaction between 9-Bromotriptycene (7; X = Br, Y = H)[a–d] as well as some 9,10-Dihalotriptycenes (7; X = Y = Halogen) and $Me_3SnLi$ in THF**

| entry no. | compd | additive | product distribution proportions, % | | | | | | | | extent of reaction, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | HTrH | ClTrH | BrTrH | SnTrH | ClTrSn | BrTrSn | ITrSn | SnTrSn | |
| 1 | **7**; X = Br, Y = H | none | 10 (9) | | | 90 (91) | | | | | 100 |
| 2 | **7**; X = Br, Y = H | TBA | 82 (84) | | | 18 (16) | | | | | 100 |
| 3 | **7**; X = Br, Y = H | DCHP | (56) | | | (44) | | | | | 100 |
| 4 | **7**; X = Br, Y = Br | none | t (t) | | 3 (4) | 5 (4) | | 66 (62) | | 26 (30) | 100 |
| 5 | **7**; X = Br, Y = Br | TBA | 28 (26) | | 52 (48) | 16 (18) | | 4 (8) | | | 88 |
| 6 | **7**; X = Br, Y = Br | DCHP | (16) | | (64) | (20) | | | | | 100 |
| 7 | **7**; X = Br, Y = I | none | 9 (9) | | 19 (18) | | | 53 (57) | 19 (16) | | 90 |
| 8 | **7**; X = Br, Y = I | none | 5 (13) | | | 30 (41) | | | | 65 (46) | 100 |
| 9 | **7**; X = Br, Y = I | TBA | 58 (62) | | 27 (22) | 14 (16) | | | | 1 (0) | 100 |
| 10 | **7**; X = Br, Y = I | DCHP | (24) | | (34) | (21) | | (21) | | | 100 |
| 11 | **7**; X = Cl, Y = Br | none | 3 (5) | 24 (24) | | 12 (11) | 51 (51) | | | 10 (9) | 100 |
| 12 | **7**; X = Cl, Y = Br | TBA | 17 (18) | 67 (66) | | 5 (5) | 11 (11) | | | | 100 |

[a] Product proportions determined by $^{13}C$ NMR and VPC. The results of the latter are listed in parentheses. See footnotes a–c of Table 1 as well as footnote a of Table 2. [b] Two molar equivalents of $Me_3SnLi$ was used in all reactions except for entry 7. One molar equivalent was used for the latter. [c] HTrH ≡ triptycene, Sn = $SnMe_3$. [d] t = trace.

**9,10-Dihalotriptycenes (7).** Product distributions for the trimethylstannylation of 9-bromotriptycene (**7**, X = Br, Y = H) and some 9,10-dihalotriptycenes (**7**, X = Br, Y = Br; X = Br, Y = I; X = Cl, Y = Br) in the absence and presence of trapping agents (DCPH and TBA) are set out in Table 4. The mixtures were all fully characterized by $^{13}C$ and $^{119}Sn$ and vpc. The availability of authentic samples from previous work facilitated the analyses.[27] It can be seen that the product mixtures (substitution versus reduction) are markedly affected in the presence of both trapping agents. The yield of reduction products in the presence of TBA demonstrates that a carbanion mediated pathway is clearly dominant. On the basis of the reasonable assumption that TBA is functioning with unit efficiency,[8,10] the result for **7** (X = Br, Y = H; entries 1 and 2) permits a semiquantitative apportioning of the two competing mechanisms (carbanion (>80%), radical (<20%)). No such deduction can be drawn from the DCPH data as this efficient trapping agent of alkyl radicals is also known to scavenge carbanions.[6]

Given that most derivatives of **2** react with $Me_3SnLi$ predominantly by a polar mechanism[8,10](see Introduction), and moreover, given that the efficiency of lithium–halogen exchange at the bridgehead of polycyclic alkanes appears to be inversely proportional to the stability of the bridgehead radical[16a,28] (the stability of the 9-triptycyl and bicyclo[2.2.1]hept-1-yl radicals are comparable)[29] the dominance of the polar mechanism for the halotriptycenes (**7**) is not surprising. However, it is of interest to note that the latter situation contrasts with a study by Rossi et al.[30] that **7** (X = Br, Y = H) and **7** (X = Y = Br) react with diphenylphosphine anions under photostimulation in liquid ammonia to yield substitution products via an $S_{RN}1$ reaction.

A pertinent distinction between the results of trimethylstannylation of the dihalo derivatives of **2**[8] and **7** is that whereas the nucleofugality of the halogens for the former are anomalous those for the latter conform with the accepted order (I > Br ≫ Cl). In this regard, note (see Table 4) the relative amounts of the bromo and iodo tin derivatives (BrTrSn > ITrSn) obtained from the bromo iodide (**7**, X = Br, Y = I; entry 7) and the exclusive formation of the chloro tin compound (ClTrSn) from the chloro bromide (7, X = Cl, Y = Br; entry 11). This difference between these two systems which exhibit similar angular strains at the respective bridgeheads[29c] corroborates our explanation for the anomalous nucleofugality of the halogens for **2**, namely, that [2.2.1]-propellane must be an intermediate in the trimethylstannylation reactions of **2**.[8] In the case of **7**, it has been clearly demonstrated that structural constraints preclude the decomposition of 9-halo-10-triptycyllithium species (**7**, X = halogen, Y = Li) to a propellane.[31] This distinction between **2** and **7** also clearly explains why the product distribution of **7** (entry 4, BrTrSn > SnTrSn) contrasts with the corresponding result for **2**. The latter yields predominantly the ditin compound with only a trace of the bromo tin substitution product even on treatment with less than 1molar equiv of $Me_3SnLi$.

## Conclusion

The above results coupled with those previously reported[7–10] clearly demonstrate that treatment of halo

(27) Adcock, W.; Iyer, V. S. *Magn. Reson. Chem*. **1991**, *29*, 381.
(28) Paquette, L. A.; Lagerwall, D. R.; King, J. L.; Niwayama, S. *Tetrahedron Lett*. **1991**, *32*, 6529.
(29) (a) Nelsen, S. F.; Travecedo, E. F. *J. Org. Chem*. **1969**, *34*, 3651. (b) Bartlett, P. D.; Greene, F. D. *J. Am. Chem. Soc*. **1954**, *76*, 1088. (c) Skvarchenko, V. R.; Shalaev, V. K.; Klabunovskii, E. I. *Russ. Chem. Rev*. **1974**, *43*(11), 951 and references therein. (d) Walton, J. C. *Chem. Soc. Rev*. **1992**, *105* and references therein.
(30) Palacios, S. M.; Santiago, A. N.; Rossi, R. A. *J. Org. Chem*. **1984**, *49*, 4609.
(31) (a) Bohm, H.; Kalo, J.; Yarnitzky, C. H.; Ginsburg, D. *Tetrahedron* **1974**, *30*, 217. (b) Markyl, G.; Mayr, A. *Tetrahedron Lett*. **1974**, *20*, 1817.

bridgehead-substituted polycyclic alkanes with $Me_3Sn^-$ can lead to either free-radical or carbanion intermediates. The former mediate tin substitution by an $S_{RN}1$-type mechanism. The latter can also lead to tin substitution products, but this may be either a direct or an indirect (via propellane formation) process depending on the polycyclic alkane and the disposition of the leaving groups with respect to the substituent. In many instances, there is a clear competition between the radical and polar reaction pathways that is delicately balanced. The main molecular factors governing this situation are the nature of the leaving groups, the angular strain at the bridgehead of the polycyclic alkane, and substituent effects. The latter appear to be particularly important if a significant through-space or through-bond electron delocalization interaction is induced as a result of appropriate orbital alignments. Whether the bifurcation of the radical and polar reaction pathways proceeds from electron-transfer in a common TS or an intermediate remains an open question. It is of interest to note that radical and polar reaction pathways have been identified for the reaction between triorganostannyl anions and haloarenes.[32] A competition between these pathways is also possible here depending on the following variables: (i) structure of the tin nucleophile, (ii) the nature of the halogens, (iii) the aromatic substrate, (iv) disposition of substituents, and (v) experimental conditions (thermal or light-induced).

## Experimental Section

**Compounds.** General methods were the same as described in recent papers.[9,10,19,33] Adamantane and adamantan-2-one were purchased from the Aldrich Chemical Co., Inc. Except for the iodo and tin derivatives (**4/5**, Y = H, X = I and $Me_3$-Sn), all the required 2-substituted (X) adamantanes (**4/5**, Y = H, X = OH,[33] COOH,[34] Cl,[35] and Br[35]) were prepared by literature procedures. The former compound was prepared from the corresponding acid (**4/5**, Y = H, X = COOH) by use of an iododecarboxylation procedure previously described for the preparation of 1-chloro-3-iodadamantane (**3**, X = Cl, Y = I).[9] The latter was prepared by treating the corresponding bromo compound (**4/5**, Y = H, X = Br) with $Me_3SnLi$ in a standard way.[7] The physical properties[33−35] and $^{13}C$ NMR data[36−38] of these compounds were in accord with the literature values. The 1-substituted (X) adamantanes (**3**, Y = H, X = Cl, Br, I, and $SnMe_3$) were available from a previous study[9] as was (*E*)- and (*Z*)-2-chloro(or -bromo)trimethylstannyl-5-(trimethylstannyl)adamantanes (**4** and **5**, X = Cl, Br, and $SnMe_3$, Y = $SnMe_3$, respectively)[12] and the (*E*)- and (*Z*)-5-(trimethylstannyl)-adamantan-2-ols (**4** and **5**, X = OH and Y = $SnMe_3$, respectively).[17,18a] The 5-substituted (X) adamantan-2-ones (**6**, Y = O, X = COOH,[39] X = $COOCH_3$,[39] Br,[40] I,[18a] $SnMe_3$[18a]), 5-substituted(X)-2-methyleneadamantanes (**6**, Y = $CH_2$, X = H, Br, I, $SnMe_3$),[33] and the halotriptycenes (**7**, X = Br, Y = H; X = Y = Br; X = Cl, Y = Br)[41] were prepared by literature procedures as previously described or indicated. The syntheses of the (*E*)- and (*Z*)-2,5(or 1,4)-dihaloadamantanes (**4** and **5**, X = Cl, Y = Br; X = Cl, Y = I; X = Y = Br; X = Br, Y = I) and 9-bromo-10-iodotriptycene (**7**, X = Br, Y = I) are described below.

**(*E*)- and (*Z*)-1-Bromo-4-chloroadamantanes (4 and 5; X = Cl and Y = Br, respectively) and (*E*)- and (*Z*)-2-Chloro-5-iodoadamantane (4 and 5; X = Cl and Y = I, respectively).** A solution of methyl 4-oxoadamantane-1-carboxylate (**6**, X = $COOCH_3$, Y = O; 1.0 g, 4.81 mmol) in methanol (2.5 mL) was added dropwise to a vigorously stirred solution of sodium borohydride (1.82 g, 48.1 mmol) maintained at 0 °C. After the reaction mixture was allowed to stir at this temperature for 2.5 h, dilute hydrochloric acid (1%, 78 mL) was added to quench the reaction. The reaction mixture was thoroughly extracted with ether (3 × 1) and the combined extracts were then washed with aqueous saturated sodium carbonate (1×) and then water (1×) before being dried over magnesium sulfate. The solvent was removed in vacuo to afford a colorless viscous oil (0.79 g, 78%). A $^{13}C$ NMR analysis indicated a 56/44 (*E*/*Z*) mixture of the epimeric alcohols (**4** and **5**; X = OH and Y = $COOCH_3$). The $^{13}C$ NMR spectra were in accord with those previously reported.[33]

By use of a procedure similar to that of Lantvoev,[42] a solution of the *E*/*Z* epimeric alcohols (**4** and **5**; X = OH and Y = $COOCH_3$; 3.41 g, 1.60 mmol) and triphenylphosphine (10.33 g, 39.4 mmol) in tetrachloromethane (100 mL) was refluxed for 72 h. The reaction mixture was cooled and filtered, and the solvent was removed in vacuo to afford a crude residue that was extracted with ether. The solvent was evaporated in vacuo and the residue chromatographed (silica gel; 10% ethyl acetate/hexane as eluent) to remove all traces of triphenylphosphine. Separation of the epimeric chloro ester mixture (**4** and **5**; X = Cl and Y = $COOCH_3$; *E*/*Z* = 35/65) was effected by HPLC (prepacked silica gel column) with 1.5% ethyl acetate/hexane as the eluent. The compounds were obtained as colorless oils (2.56 g (combined yield), 69%). *E* isomer (**4**, X = Cl, Y = $COOCH_3$): $^{13}C$ NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 39.60 (C1), 39.25 (C2,9), 35.13 (C3,5), 66.23 (C4), 29.79 (C6,10), 27.04 (C7), 38.94 (C8), 51.69 ($CH_3$), 177.0 (CO). Z isomer (**5**, X = Cl, Y = $COOCH_3$): $^{13}C$ NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 39.85 (C1), 32.00 (C2,9), 35.42 (C3,5), 65.76 (C4), 36.67 (C6,10), 26.31 (C7), 38.76 (C8), 51.43 ($CH_3$), 176.91 (CO). Hydrolysis of both esters by a standard procedure ($KOH/C_2H_5OH/H_2O$) afforded the corresponding 4-chloroadamantane-1-carboxylic acids as white solids upon sublimation. *E* isomer (**4**, X = Cl, Y = COOH): mp 175−177 °C (lit.[42] mp 183−185 °C); $^{13}C$ NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 39.49 (C1), 38.96 (C2,9), 35.00 (C3,5), 66.05 (C4), 29.74 (C6,10), 26.93 (C7), 38.67 (C8), 183.56 (CO). *Z* isomer (**5**, X = Cl, Y = COOH): mp 174−176 °C (lit.[42] mp 183−185 °C); $^{13}C$ NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 39.94 (C1), 31.93 (C2,9), 35.51 (C3,5), 65.83 (C4), 36.83 (C6,10), 26.40 (C7), 38.72 (C8), 183.60 (CO).

**(*E*)-1-Bromo-4-chloroadamantanes (4 and 5; X = Cl and Y = Br).** Following procedures recently described for the preparation of 1-bromo-3-chloroadamantane (**3**; X = Br and Y = Cl) from 3-chloroadamantane-1-carboxylic acid (**3**, X = COOH and Y = Cl),[9] (*E*)-4-chloroadamantane-1-carboxylic acid (**4**, X = Cl and Y = COOH; 1.0 g, 4.66 mmol) was converted into the title compound, which on sublimation afforded a white solid (860 mg, 74%). Recrystallization from methanol gave the (*E*)-bromo chloride as colorless crystals: mp 134−136 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.56 (2H, d), 2.09 (1H, s), 2.21 (2H, s), 2.28 (2H, d), 2.37 (2H, s), 2.44 (4H, s), 4.36 (1H, s); $^{13}C$ NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 61.92 (C1), 48.92 (C2,9), 39.16 (C3,5), 64.72 (C4), 29.08 (C6,10), 31.47 (C7), 49.21 (C8); MS *m*/*z* ($M^+$) calcd for $C_{10}H_{14}BrCl$ 169.0784, 171.05694, found 169.0812, 171.0781.

**(Z)-1-Bromo-4-chloroadamantane (5; X = Cl and Y = Br).** Following procedures indicated above for the preparation of the *E*-isomer, (*Z*)-4-chloroadamantane-1-carboxylic acid (**5**, X = Cl and Y = COOH; 1.0 g, 4.66 mmol) was converted into the title compound. Sublimation gave a white solid (990 mg, 85%) that was recrystallized from methanol to afford the (*Z*)-

(32) Yammal, C. C.; Podestá, J. C.; Rossi, R. A. *J. Org. Chem*. **1992**, *57*, 5720.
(33) Adcock, W.; Cotton, J.; Trout, N. A. *J. Org. Chem*. **1994**, *59*, 1867.
(34) Udding, A. C.; Strating, J.; Wynberg, H. *Tetrahedron Lett*. **1968**, 1345.
(35) Farcasiu, D. *Synthesis* **1972**, 615.
(36) Hoek, W.; Strating, J.; Wynberg, H. *Rec. Trav. Chim*. **1966**, *85*, 1045.
(37) Krishnamurthy, V. V. Iyer, P. S.; Olah, G. A. *J. Org. Chem*. **1983**, *48*, 3373.
(38) Kuivila, H. G. *J. Organomet. Chem*. **1976**, *111*, 179.
(39) Lantvoev, V. I. *J. Org. Chem. U.S.S.R. (Engl. Trans.)* **1976**, *12*, 2292.
(40) Geluk, H. W.; Schlatmann, M. A. *Tetrahedron* **1968**, *24*, 5369.
(41) (a) Adcock, W.; Iyer, V. S. *J. Org. Chem*. **1988**, *53*, 5259. (b) Adcock, W.; Iyer, V. S. *Magn. Reson. Chem*. **1991**, *29*, 381.
(42) Lantvoev, V. I. *Zh. Organ. Khim*. **1980**, *16*, 1659.

bromo chloride as colorless crystals: mp 127−128.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.79 (2H, d), 1.91 (2H, s), 2.07 (1H, m), 2.16 (2H, d), 2.26 (2H, s), 2.34 (2H, s) 2.86 (2H, d), 4.28 (1H, s); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 63.14 (C1), 36.0 (C2,9), 39.80 (C3,5), 64.38 (C4), 42.34 (C6,10), 30.76 (C7), 49.09 (C8); MS *m*/*z* ($M^+$) calcd for $C_{10}H_{14}BrCl$ 169.0784, 171.05694, found 169.0813, 171.0840.

**(*E*)-2-Chloro-5-iodoadamantane (4; X = Cl and Y = I).** Following procedures recently described for the preparation of 1-chloro-3-iodoadamantane (**3**, X = Cl and Y = I) from 3-chloroadamantane-1-carboxylic acid (**3**, X = Cl, Y = COOH)[9] (*E*)-4-chloroadamantane-1-carboxylic acid (**4**, X = Cl and Y = COOH; 1.0 g, 4.66 mmol) was converted into the title compound. Sublimation gave a white solid (980 mg, 84%) that was recrystallized from methanol to afford the (*E*)-chloro iodide as colorless crystals: mp 115−116.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.63 (2H, d), 1.93 (1H, s), 2.07 (2H, s), 2.36 (2H, d), 2.66 (6H, m), 4.40 (1H, s); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 39.80 (C1,3), 64.93 (C2), 52.10 (C4,9), 44.42 (C5), 52.24 (C6), 31.91 (C7), 29.11 (C8,10); MS *m*/*z* ($M^+ - I$) calcd for $C_{10}H_{14}ClI$ 169.0784, 171.05694, found 169.0759, 171.0869.

**(*Z*)-2-Chloro-5-iodoadamantane (5; X = Cl and Y = I).** Following procedures indicated above for the preparation of the *E*-isomer, (*Z*)-4-chloroadamantane-1-carboxylic acid (**5**, X = Cl and Y = COOH; 1.0 g, 4.66 mmol) was converted into the title compound. Sublimation gave a white solid (950 mg, 82%) that was recrystallized from methanol to afford the (*Z*)-chloro iodide as colorless crystals: mp 71−72.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.88 (2H, d), 1.90 (1H, s), 2.00 (2H, d), 2.11 (2H, s), 2.42 (2H, d), 2.61 (2H, s), 3.10 (2H, d), 4.38 (1H, s); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 40.00 (C1,3), 64.51 (C2), 45.30 (C4,9), 45.85 (C5), 52.18 (C6), 31.16 (C7), 36.02 (C8,10); MS *m*/*z* ($M - I^+$) calcd for $C_{10}H_{14}ClI$ 169.0784, 171.05694, found 169.0795, 171.0757.

**(*E*)- and (*Z*)-1,4-Dibromoadamantane (4 and 5; X = Y = Br) and (*E*)- and (*Z*)-2-Bromo-5-iodoadamantane (4 and 5; X = Br and Y = I, respectively).** By use of the procedure of Lantvoev,[42] a solution of tetrabromomethane (3.42 g, 7.32 mmol) in dry THF (10 mL) was added dropwise to a solution of the *E*/*Z* epimeric alcohols (**4** and **5**; X = OH and Y = $COOCH_3$; 1.44 g, 6.9 mmol) and triphenylphosphine (1.92 g, 7.32 mmol) in dry THF (20 mL). The reaction mixture was refluxed for 72 h and then worked up as described above for the corresponding chloro esters. Separation of the epimeric bromo-ester mixture (**4** and **5**; X = Br and Y = $COOCH_3$; *E*/*Z* = 35/65) was effected by HPLC (prepacked silica gel column) with 1.5% ethyl acetate/hexane as the eluent. The compounds were obtained as colorless oils (1.11 g (combined yield), 59%). *E* isomer (**4**, X = Br and Y = $COOCH_3$): $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 35.67 (C1,3), 61.15 (C2), 39.74 (C4,9), 39.64 (C5), 39.12 (C6), 27.15 (C7), 30.52 (C8,10), 51.75 ($CH_3$), 176.69 (CO). *Z* isomer (**5**, X = Br, Y = $COOCH_3$): $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 35.53 (C1,3), 60.64 (C2), 32.53 (C4,9), 39.79 (C5), 38.81 (C6), 26.25 (C7), 37.12 (C8,10), 51.28 ($CH_3$), 176.54 (CO). Hydrolysis of both esters by a standard procedure (KOH/$C_2H_5OH$/$H_2O$) afforded the corresponding 4-bromoadamantane-1-carboxylic acids as white solids upon sublimation. *E* isomer (**4**, X = Br and Y = COOH): mp 174−176 °C (lit.[42] mp 195−197 °C); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 35.54 (C1,3), 60.86 (C2), 39.47 (C4,9), 39.53 (C5), 38.87 (C6), 27.05 (C7), 30.46 (C8,10), 183.41 (CO). *Z* isomer (**5**, X = Br and Y = COOH): mp 186−188 °C (lit.[42] mp 198−199 °C); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 36.10 (C1,3), 60.76 (C2), 32.62 (C4,9), 40.06 (C5), 38.92 (C6), 26.48 (C7), 37.43 (C8,10), 183.50 (CO).

**(*E*)-1,4-Dibromoadamantane (4; X = Y = Br).** Following procedures indicated above for the preparation of (*E*)-1-bromo-4-chloroadamantane (**4**; X = Cl and Y = Br), (*E*)-4-bromoadamantane-1-carboxylic acid (4, X = Br and Y = COOH; 1.0 g, 3.86 mmol) was converted into the title compound. Sublimation gave a white solid (900 mg, 87%) that was recrystallized from methanol to afford the (*E*)-dibromide as colorless crystals: mp 143−144.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.62 (2H, d), 2.11 (1H, s), 2.31 (2H, d), 2.39 (4H, s), 2.49 (4H, s), 4.59 (1H, s); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 61.86 (C1), 49.43 (C2,9), 39.72 (C3,5), 59.13 (C4), 29.78 (C6,10), 31.54 (C7), 49.35 (C8); MS *m*/*z* ($M^+ - Br$) calcd for $C_{10}H_{14}Br_2$ 213.02785, 215.02585, found 213.0244, 215.0221.

**(*Z*)-1,4-Dibromoadamantane (5; X = Y = Br).** Following procedures indicated above for the preparation of the *E*-isomer, (*Z*)-4-bromoadamantane-1-carboxylic acid (**5**, X = Br and Y = COOH; 1.0 g, 3.86 mmol) was converted to the title compound. Sublimation gave a white solid (850 mg, 75%) that was recrystallized from methanol to afford the (*Z*)-dibromide as colorless crystals: mp 106−108 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.86 (2H, d), 1.96 (2H, d), 2.12 (1H, s), 2.22 (2H, d), 2.34 (2H, d), 2.36 (2H, s), 2.94 (2H, d), 4.54 (1H, s); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 63.13 (C1), 42.98 (C2,9), 40.35 (C3,5), 58.91 (C4), 36.59 (C6,10), 30.79 (C7), 49.24 (C8); MS *m*/*z* ($M^+ - Br$) calcd for $C_{10}H_{14}Br_2$ 213.02785, 215.02585, found 213.0255, 215.0256.

**(*E*)-2-Bromo-5-iodoadamantane (4, X = Br and Y = I).** Following procedures indicated above for the preparation of (*E*)-2-chloro-5-iodoadamantane (**4**; X = Cl and Y = I), (*E*)-4-bromoadamantane-1-carboxylic acid (**4**, X = Br and Y = COOH; 1.0 g, 3.86 mmol) was converted into the title compound. Sublimation gave a white solid (750 mg, 63%) that was recrystallized from methanol to afford the *E*-bromo iodide as colorless crystals: mp 127−129 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.68 (2H, d), 1.94 (1H, s), 2.14 (2H, s), 2.44 (2H, d), 2.63 (2H, s), 2.73 (4H, s); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 40.38 (C1,3), 59.50 (C2), 52.64 (C4,9), 44.34 (C5), 52.44 (C6), 32.01 (C7), 29.85 (C8,10); MS *m*/*z* ($M^+ - I$) calcd for $C_{10}H_{14}BrI$ 213.02785, found 213.02785.

**(*Z*)-2-Bromo-5-iodoadamantane (5, X = Br and Y = I).** Following thprocedures indicated above for the preparation of the *E*-isomer, (*Z*)-4-bromoadamantane-1-carboxylic acid (**5**, X = Br and Y = COOH; 1.0 g, 3.86 mmol) was converted to the title compound. Sublimation gave a white solid (880 mg, 89%) that was recrystallized from methanol to afford the *Z*-bromo iodide as colorless crystals: mp 86−87.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.99 (5H, m), 2.17 (2H, s), 2.46 (2H, d), 2.62 (2H, s), 3.18 (2H, d), 4.63 (1H, s); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 40.52 (C1,3), 59.13 (C2), 45.92 (C4,9), 45.82 (C5), 52.34 (C6), 31.19 (C7), 36.82 (C8,10); MS *m*/*z* ($M^+ - I$) calcd for $C_{10}H_{14}BrI$ 213.02785, found 213.0295.

**9-Bromo-10-iodotriptycene (7; X = Br and Y = I).** By use of the lithiation procedure of Kawada and Iwamura,[43] a solution of 9,10-dibromotriptycene (**7**, X = Y = Br; 5.0 g, 0.012 mol) in benzene/diethyl ether (100 mL; 1:2 v/v) was treated with ca. 2.2 molar equiv of *n*-butyllithium (25 mL of 1 M solution in hexane; 0.026 mol) at 0 °C under an atmosphere of dry nitrogen. The reaction mixture was stirred at this temperature for 30 min and then allowed to stand undisturbed for 1 h after removal of the cold bath. The supernatant liquid was carefully removed by syringe under nitrogen before freshly distilled iodobenzene (9.9 g, 0.05 mol) was added to the 9-bromo-10-triptycyllithium (**7**; X = Br and Y = Li) and the reaction mixture refluxed overnight. After cooling the reaction mixture was quenched with saturated aqueous $NH_4Cl$ and worked up in the standard manner. Recrystallization from a hexane/ethanol mixture (1:1 v/v) afforded the title compound as leaflets (3.5 g, 64%): mp 303−305 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.03−7.26 (6H, m, Ar), 7.83−8.06 (6H, m, Ar); $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 123.26 (C1,8,13), 126.68 (C2,7,-14), 126.59 (C3,6,15), 127.81 (C4,5,16), 142.28 (C4a,10a,11), 143.63 (C8a,9a,12), 71.73 (C9), 59.59 (C10); MS *m*/*z* ($M^+$) calcd for $C_{20}H_{12}BrI$ 457.91695, 459.91498, found 457.9196, 459.9165.

**Conversion of 6 (X = COOH, Y = O) to 6 (X = Br, Y = O).** Following procedures recently described for the preparation of 1-bromo-3-chloroadamantane (**3**; X = Br and Y = Cl) from 3-chloroadamantane-1-carboxylic acid (**3**, X = COOH and Y = Cl),[9] **6** (X = COOH, Y = O; 0.5 g, 2.58 mmol) was converted to **6** (X = Br, Y = O). A vpc and GC/MS analysis of the crude product revealed the complete absence of the fragmentation product (**11**). Sublimation of the crude product gave **6** (X =

(43) (a) Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1981**, *46*, 3357. (b) Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1983**, *105*, 1449.

Br, Y = O) as a white solid (0.47 g, 80%): mp 150−152 °C (lit.[40] mp 150−154 °C).

**Trimethylstannylation Procedures.** These were identical with those previously described for the stannylation of the 1,3-dihaloadamantanes (**3**)[9] and the 1,4-dihalobicyclo[2.2.2]-octanes (**1**).[7] The former procedure was used for the haloadamantanes (**4** and **5**) and halotriptycenes (**7**), while the latter was employed for the haloadamantanones (**6**, Y = O) and methylenehaloadamantanes (**6**, Y = $CH_2$). A preparative-scale reaction was carried out on 5-iodoadamantan-2-one (**6**, X = I and Y = O) as follows: A solution of the iodo ketone (**6**, X = I and Y = O; 0.8 g, 2.9 mmol) in THF (6 mL) was treated with $Me_3SnLi$ (3 molar equiv), and the reaction was worked up in the usual manner to afford a pale yellow oil (1.5 g). VPC analysis of the crude product indicated a mixture containing predominantly hexamethylditin and two other components in the ratio 94/6. No unreacted starting material (**6**, X = I and Y = O) was detected. A careful Kugelrohr distillation (Büchi: GKR-50) of the mixture led to the removal of the hexamethylditin, and a colorless liquid fraction (0.30 g) was obtained. GC/MS and VPC indicated that the minor components of the latter distillate was adamantan-2-one. A combination of GC/MS, NMR, and IR established the identity of the major product as being 7-methylenebicyclo[3.3.1]nonan-2-one (**11**):[21] $^1$H NMR ($CDCl_3$) $\delta$ 4.66, 4.50, 2.5−1.8; $^{13}$C NMR ($CDCl_3$, relative to $Me_4$-Si) $\delta$ 47.51 (C1), 214.25 (C2), 33.27 (C3), 30.96 (C4), 28.29 (C5), 38.47 (C6), 145.74 (C7), 40.16 (C8), 37.84 (C9), 110.85 (C10); IR (film) 3053, 1701, 1648, 891 cm$^{-1}$; MS ($M^+$) cald for $C_{10}H_{14}O$ 150.10446, found 150.1049.

As indicated above the 2-chloro and -bromo-5-(trimethylstannyl)adamantanes (**4** and **5**; X = Cl and Br, Y = $SnMe_3$) have been previously reported.[12] The corresponding iodo-tin compounds (**4** and **5**; X = I and Y = $SnMe_3$) were identified as minor components in the trimethylstannylation reactions of the chloro iodides (**4** and **5**, X = Cl and Y = I; see entries 7, 8, 10, and 11 of Table 1) and bromo iodides (**4** and **5**, X = Y = Br; see entries 19, 20, 22, and 23 of Table 1) by $^{13}$C and $^{119}$Sn NMR, GC/MS, and VPC. (*E*)-2-Iodo-5-(trimethylstannyl)adamantane (**4**, X = I and Y = $SnMe_3$): $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 38.88 (C1,3), 47.77 (C2), 43.34 (C4,9), n.o (C5), 42.70 (C6), 28.90 (C7), 33.17 (C8,10); $^{119}$Sn NMR ($CDCl_3$ relative to $Me_4Sn$) $\delta$ 0.80. (*Z*)-2-Iodo-5-(trimethylstannyl)-adamantane (**5**, X = I and Y = $SnMe_3$): $^{13}$C NMR ($CDCl_3$, relative to $Me_4Si$) $\delta$ 38.53 (C1,3), 47.50 (C2), 37.42 (C4,9), n.o (C5), 42.77 (C6), 27.91 (C7), 38.95 (C8,10); $^{119}$Sn NMR ($CDCl_3$ relative to $Me_4Sn$) $\delta$ −2.42. The $^{13}$C NMR spectra were assigned by additivity methodology. *E*-isomer (calcd): 38.40 (C1,3), 46.78 (C2), 43.22 (C4,9), 26.91 (C5), 42.56 (C6), 28.55 (C7), 33.12 (C8,10). *Z*-isomer (calcd): 38.40 (C1,3), 46.78 (C2), 37.41 (C4,9), 27.58 (C5), 42.56 (C6), 27.88 (C7), 38.93 (C8,10).

**Acknowledgment.** We are grateful to the Australian Research Council for partial financial support of this work. We thank Dr. V. Sankar Iyer for assistance with some of the preliminary studies on this investigation.

JO001638W