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Reactions of 1- and 2-Halo- and 1,2-Dichloroadamantanes with Nucleophiles by the $S_{RN}1$ Mechanism

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2-Bromoadamantane (2-BrAd) reacted in liquid ammonia under irradiation with diphenylphosphide (Ph_2P^-) ions whereas 2-chloroadamantane (2-ClAd) did not under the same experimental conditions. However, 2-ClAd yielded 2-(trimethylstannyl)adamantane in its photostimulated reaction with trimethylstannyl (Me_3Sn^-) ions. The compound 1-ClAd yielded the substitution product in a photostimulated slow reaction when the nucleophile is Ph_2P^- ion; the reaction occurs faster with the nucleophile Me_3Sn^- ion. All these reactions can be explained by the $S_{RN}1$ mechanism as they did not occur in the dark and were inhibited by *p*-dinitrobenzene when photostimulated. In competition experiments, 1-haloadamantane showed more reactivity than 2-haloadamantane. Either with Ph_2P^- or Me_3Sn^- ions, 1-BrAd is 1.4 times more reactive than 2-BrAd while 1-ClAd is 12 times more reactive than 2-ClAd with Me_3Sn^- ions. In the photostimulated reaction of 1,2-dichloroadamantane (**7**) with Ph_2P^- the monosubstitution products 1-adamantyldiphenylphosphine (64%) and 2-adamantyldiphenylphosphine (15%) were formed, isolated as the oxides. From these results, it appears that when **7** receives an electron, the 1-position fragments *ca.* four times faster than the 2-position. The disubstitution product was not formed with Ph_2P^- ions, but when **7** reacted with a nucleophile having less steric bulk such as a Me_3Sn^- ion, the 2-chloro-1-(trimethylstannyl)-adamantane and the disubstitution product 1,2-bis(trimethylstannyl)adamantane were formed. The formation of these products is explained in terms of the different rates of the electron transfer reactions of the radical anion intermediates.

Several alkyl halides have been found to react with nucleophiles by the radical nucleophilic substitution, or $S_{RN}1$ mechanism.[1] The main steps are shown in eqs 1−3.

Initiation step:

$$RX + Nu^- \xrightarrow{ET} R^\bullet + X^- + Nu^\bullet \qquad (1)$$

Propagation steps:

$$R^\bullet + Nu^- \longrightarrow (RNu)^{-\bullet} \qquad (2)$$

$$(RNu)^{-\bullet} + RX \longrightarrow RNu + R^\bullet + X^- \qquad (3)$$

When there is no spontaneous electron transfer (ET) from the Nu^- to the substrate RX, the initiation step can occur under photostimulation[1] or with $FeBr_2$ in DMSO.[2] The alkyl radical $R^\bullet$ thus formed couples with the Nu^-, yielding a new radical anion $(RNu)^{-\bullet}$ (eq 2), which by an intermolecular dissociative ET[3] to the substrate gives the substitution product and the alkyl radical $R^\bullet$ to continue the chain propagation cycle (eq 3).

The alkyl halides that react by the $S_{RN}1$ mechanism are mainly those that have a relatively low reactivity toward polar nucleophilic substitution reactions. For instance, 1-haloadamantanes as well as other bridgehead halides react with Ph_2P^- ions by this mechanism.[1] The process has also been proposed in the reaction of 1-iodoadamantane (1-IAd) with carbanions,[2,4] PhS^-,[5] $PhSe^-$,[5] and $PhTe^-$ [5] ions. Recently, it has been demonstrated that the photostimulated reaction of 1-IAd with arenethiolate ions occurs by a nonchain $S_{RN}1$ reaction.[6] On the other hand the trimethylstannylation of 1-BrAd and 1-IAd with $NaMe_3Sn$ in THF at 0 °C proceeds predominantly by a free radical process.[7] Other alkyl halides[8] and other bridgehead halides[9] have been proposed to react with Me_3Sn^- ions by electron transfer.

The $S_{RN}1$ reactions of dihalo bridgehead compounds with nucleophiles give either the monosubstitution or disubstitution product depending on the radical type, the nature of the nucleofugal group, or the nucleophile.[10,11] The monosubstitution product is not an intermediate in the formation of the disubstitution one. For example, in the $S_{RN}1$ photostimulated reaction of 1,3-dihaloadaman-

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tanes with Ph_2P^- ions mainly the disubstitution product is formed.[12] In the reaction of 1,3-dihaloadamantanes with $NaMe_3Sn$ in THF at 0 °C, the products depend on the leaving groups. Thus, when the halides are iodides or bromides the reaction proceeds predominantly with the formation of 1,3-adamantene, but with chlorides or 1-chloro-3-bromo, the disubstitution product is formed through the $S_{RN}1$ mechanism.[13] Besides, Adcock et al. reported that trimethylstannylation of dihalo bridgehead compounds in THF at 0 °C proceed between two pathways (radical or polar process).[14]

Although the 2-position of the adamantane system is a secondary carbon atom of a cyclohexane system, it shows a lower reactivity than the 1-position toward nucleophiles in polar reactions. It has been reported that 1-adamantyl tosylate solvolyzes about 10^5 times faster than 2-adamantyl tosylate.[15] Besides, chloro and bromo cyclohexanes and derivatives react under irradiation with Ph_2P^- ions in liquid ammonia by the $S_{RN}1$ mechanism.[16]

The reaction of 2-chloro-5-iodoadamantane (*E* and *Z*) with $LiMe_3Sn$ in THF at 0 °C gave mainly the reduction product 2-ClAd and the monosubstitution compound 2-chloro-5-(trimethylstannyl)adamantane, but in the reaction with 2-bromo-5-iodoadamantane (*E* and *Z*), the disubstitution product is obtained in high yield. 2-Bromo-5-fluoroadamantane (*E* and *Z*) gave the monosubstitution product 2-(trimethylstannyl)-5-fluoroadamantane. On the basis of trapping experiments with dicyclohexylphosphine, these reactions were proposed to occur by the $S_{RN}1$ mechanism.[17]

Tabushi et al. reported, in the free-radical halogenation of adamantane, that the bridgehead position has a higher reactivity than the bridge position (or secondary position). They also claim that the 1-adamantyl radical is formed easily and has a longer lifetime than the 2-adamantyl radical, suggesting that it may be considerably more stable than the latter radical.[18]

On account of the previous findings we desired to undertake the study of the reactions of 1-halo-, 2-halo-, and 1,2-dihaloadamantanes with Ph_2P^- and Me_3Sn^- ions under $S_{RN}1$ conditions in order to get more insights on the relative $S_{RN}1$ reactivities of the 1- and 2-positions of halo- and dihaloadamantanes.

Results and Discussion

Reactions of 1- or 2-Haloadamantanes with Diphenylphosphide and with Trimethyltin Ions. 2-BrAd (**1**) reacts slowly with Ph_2P^- ions in liquid ammonia under dark conditions to afford the substitution product **2**, isolated as the oxide. The reaction is accelerated by irradiation (eq 4). The facts that the reactions are light catalyzed and that the photostimulated and dark reactions are inhibited by *p*-dinitrobenzene (*p*-DNB), a well known inhibitor of $S_{RN}1$ reactions,[1] suggest that they occur by this mechanism (Table 1, experiments 5−8). The slow dark reaction was completely inhibited by *p*-DNB, indicating that there is a spontaneous ET from the nucleophile to the substrate.

Table 1. Reaction of 1- and 2-Haloadamantanes with Ph_2P^- and Me_3Sn^- Ions in Liquid Ammonia

				products, % yield[a]	
expt	substrate ($\times 10^3$ M)	nucleophile ($\times 10^3$)	conditions	X^-	subst product
1[b]	1-BrAd (7.20)	Ph_2P^- (5.80)	*hν*, 20 min	100	1-AdP(O)Ph_2, 70
2	1-ClAd (2.67)	Ph_2P^- (2.95)	*hν*, 4 h	39	1-AdP(O)Ph_2, 29
3	2-ClAd (2.67)	Ph_2P^- (3.40)	*hν*, 4 h	17	1-AdP(O)Ph_2[c]
4	2-ClAd (2.67)	Ph_2P^- (3.40)	dark, 4 h	<3[d]	–
5	2-BrAd (3.30)	Ph_2P^- (3.40)	dark, 1 h	23	2-AdP(O)Ph_2[e]
6	2-BrAd (3.30)	Ph_2P^- (3.30)	dark, 1 h[f]	<1[d]	–
7	2-BrAd (3.31)	Ph_2P^- (3.33)	*hν*, 1 h	80	2-AdP(O)Ph_2, 64
8	2-BrAd (3.30)	Ph_2P^- (3.30)	*hν*, 1 h[f]	10	2-AdP(O)Ph_2, 4
9	1-ClAd (1.63)	Me_3Sn^- (1.66)	*hν*, 20 min	*e*	1-Ad$SnMe_3$, 93
10	1-ClAd (1.67)	Me_3Sn^- (1.60)	dark, 20 min	*e*	1-Ad$SnMe_3$[c]
11	1-ClAd (1.67)	Me_3Sn^- (1.70)	*hν*, 20 min[d]	*e*	1-Ad$SnMe_3$[c]
12	2-ClAd (1.66)	Me_3Sn^- (1.66)	*hν*, 75 min	*e*	2-Ad$SnMe_3$, 94
13	2-ClAd (1.68)	Me_3Sn^- (1.69)	dark, 75 min	*e*	2-Ad$SnMe_3$[c]

[a] Yields are based on substrate concentration and determined by GLC using the internal standard method. [b] See ref 29. [c] None detected. [d] The substrate was recovered unchanged. [e] Not quantified. [f] *p*-DNB was added (20 mol %).

$$\underset{\mathbf{1}}{\text{2-BrAd}} + Ph_2P^- \xrightarrow[\text{2. [O]}]{\text{1. }h\nu} \underset{\mathbf{2}}{\text{2-AdP(O)}Ph_2} + Br^- \quad (4)$$

On the other hand, in the reaction of 2-ClAd with Ph_2P^- ions only 17% yield of chloride ions was determined after 4 h of irradiation without formation of **2**. No dark reaction was observed (Table 1, experiments 3 and 4). 1-ClAd (**3**) reacts with Ph_2P^- to give 29% yield of the substitution product (Table 1, experiment 2). Thus 1-ClAd results to be more reactive than 2-ClAd in separated experiments.

Under irradiation (20 min), **3** reacts with Me_3Sn^- ions to give 93% yield of the substitution product **4** (eq 5). No reaction was found in the dark, and the photostimulated reaction was inhibited by *p*-DNB (Table 1, experiments 9−11).

$$\underset{\mathbf{3}}{\text{1-ClAd}} + Me_3Sn^- \xrightarrow[NH_3]{h\nu} \underset{\mathbf{4}}{\text{1-Ad}SnMe_3} + Cl^- \quad (5)$$

In contrast, 2-ClAd (**5**) requires a longer irradiation time (75 min) to yield 94% of substitution product **6** with Me_3Sn^- ions. In this system there is no dark reaction (Table 1, experiments 12 and 13) (eq 6).

$$\underset{\mathbf{5}}{\text{2-ClAd}} + Me_3Sn^- \xrightarrow[NH_3]{h\nu} \underset{\mathbf{6}}{\text{2-Ad}SnMe_3} + Cl^- \quad (6)$$

The fact that the reactions of **3** and **5** with Me_3Sn^- ions are light catalyzed is in agreement with the expected $S_{RN}1$ mechanism. The different irradiation times necessary to complete the reaction with this nucleophile (20 min for **3** and 75 min for **5**) show that **3** is more reactive than **5** toward Me_3Sn^- ions under these experimental conditions. The behavior observed with Ph_2P^- ions, which do not react with **5** under irradiation but react with

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Table 2. Competition Experiments of 1- and 2-Haloadamantanes with Ph_2P^- and Me_3Sn^- Ions in Liquid Ammonia

				% products, yield		
expt	1-XAd ($\times 10^3$ M)	2-XAd ($\times 10^3$ M)	nucleophile ($\times 10^3$ M)	1-AdNu	2-AdNu	k_{1-XAd}/k_{2-XAd}
1[a]	X = Br (3.33)	X = Br (3.33)	Ph_2P^- (3.33)	27[b]	19[b]	1.4
2[c]	X = Br (1.75)	X = Br (1.71)	Me_3Sn^- (1.70)	58	45	1.5
3[c]	X = Br (1.58)	X = Br (1.60)	Me_3Sn^- (1.69)	51	44	1.3
						1.4 ± 0.1 (Average)
4[a]	X = Cl (1.70)	X = Cl (1.67)	Me_3Sn^- (1.83)	80	11	13.8
5[a]	X = Cl (1.70)	X = Cl (5.00)	Me_3Sn^- (1.80)	59	8.4	10.2
6[a]	X = Cl (1.68)	X = Cl (8.33)	Me_3Sn^- (1.83)	61	7.6	12.0
						12 ± 1.2 (Average)

[a] Irradiation time 75 min. [b] Quantified as the oxides. [c] Irradiation time 15 min.

2-BrAd, reveals that the initiation step of the mechanism is not efficient between Ph_2P^- and **5**.

Competition Reactions. In order to determine the relative reactivity of 1-haloadamantanes vs 2-haloadamantanes in $S_{RN}1$ reactions, we studied their reactivity toward Me_3Sn^- and Ph_2P^- ions in competition experiments. All the reactions were performed with excess of the substrates. The relative reactivity was estimated as in previous work.[19]

When a solution containing substrates 1- and 2-BrAd is allowed to compete for Ph_2P^- ions under irradiation, from the amount of products obtained it is possible to determine that 1-BrAd is 1.4 times more reactive than 2-BrAd (Table 2, experiment 1). Similar relative reactivities were found in competitive photostimulated reactions of 1-BrAd and 2-BrAd toward Me_3Sn^- ions (Table 2, experiments 2 and 3).

A relative reactivity of 12 was determined in the competitive photostimulated reactions of 1-ClAd and 2-ClAd toward Me_3Sn^- ions (Table 2, experiments 4–6). Either with nucleophiles Me_3Sn^- or Ph_2P^-, 1-haloadamantane is more reactive than 2-haloadamantane in $S_{RN}1$ reactions, the difference in reactivity being higher with the poorest leaving group.

The relative reactivity of two substrates toward a given nucleophile will depend on the relative electron acceptor capability of the substrates toward the electron transfer reaction of eq 3, given a propagation cycle in which there are no other competing reactions. The observed relative reactivity of the compounds 1-haloadamantane and 2-haloadamantane with the same nucleophile (Ph_2P^- or Me_3Sn^-) is thus related to their reduction potential and is in agreement with the calculated σ^* MO energy of the C–X bond of the substrates.[20]

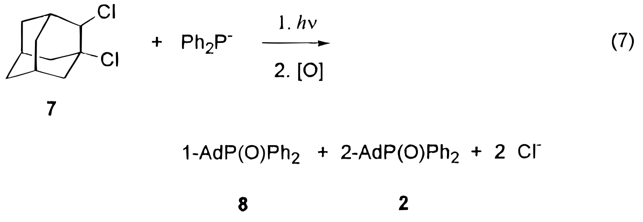
Reactions of 1,2-Dichloroadamantane with Diphenylphosphide and with Trimethyltin Ions. It has been reported that adamantene is the intermediate in the reaction of $LiPh_2P$ in THF with 1,2-diiodo- and 1,2-dibromoadamantane but not with 1,2-dichloroadamantane (**7**), although 1- and 2-adamantyldiphenylphosphine are formed in all cases, isolated as the oxides.[21]

Table 3. Reactions of 7 with Ph_2P^- and Me_3Sn^- Ions in Liquid Ammonia

expt	**7** ($\times 10^3$ M)	nucleophile ($\times 10^3$ M)	conditions	products, % yield[a]
1[b]	2.33	Ph_2P^- (4.66)	$h\nu$, 4 h	**2**, 15; **8**, 64
2	2.33	Ph_2P^- (4.66)	dark, 4 h	**2**,[c] **8**[c]
3	2.33	Ph_2P^- (4.66)	$h\nu$, 4 h[d,e]	**2**, 13; **8**, 47
4	1.70	Me_3Sn^- (3.66)	$h\nu$, 2 h	**17**, 54; **18**, 26
5	1.71	Me_3Sn^- (3.33)	dark, 2 h	**17**,[c] **18**[c]
6	1.65	Me_3Sn^- (3.40)	$h\nu$, 2 h[d]	**17**,[c] **18**[c]
7	1.69	Me_3Sn^- (11)	$h\nu$, 4 h	**17**, 50; **18**, 30
8[f]	1.20	Me_3Sn^- (1.25)	$h\nu$, 2 h	**17**, 93; **18**, <4

[a] Yields are based on substrate concentration and determined by GLC using the internal standard method. [b] Duplicate experiments. Small amounts (<4%) of adamantane, 1-ClAd and 2-ClAd were formed. [c] None detected. [d] *p*-DNB was added (20 mol %). [e] 20% of **7** was recovered. [f] The substrate was **17**.

On the other hand, when **7** reacts with Ph_2P^- ions in liquid ammonia, 92% yield of chloride ion release is determined after 240 min irradiation (based on two chlorines per molecule), together with the monosubstituted products **2** and **8** quantified as the oxides in 15% and 64% yields, respectively (eq 7). No disubstitution product 1,2-bis(diphenylphosphinyl)adamantane was found. There was no reaction in the dark after the same reaction time, and the photostimulated reaction was slightly inhibited by *p*-DNB under this experimental conditions (Table 3, experiments 1–3).



These results suggest that the reaction occurs by the $S_{RN}1$ mechanism. The nucleophile transfers one electron to the substrate in a light-catalyzed initiation step to give the haloadamantyl radicals (**9** and **10**) (eq 8) which then couple with the nucleophile to form the radical anion intermediates ($\mathbf{11}^{-\bullet}$ and $\mathbf{12}^{-\bullet}$) (eq 9). These radical anions fragment by dissociative intramolecular ET to the C–Cl bond to yield radicals **13** and **14** (eq 10). These radicals do not couple with the nucleophile probably due to a steric effect, but are reduced to products **15** or **16** (eq 11),[22] which after oxidation give the products **2** and **8**.

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[19] The equation used in the relative reactivity determination of pairs of substrates vs a nucleophile is:

$$\frac{k_s\mathbf{1}}{k_s\mathbf{2}} = \frac{\ln [S_\mathbf{1}]_0/[S_\mathbf{1}]_t}{\ln [S_\mathbf{2}]_0/[S_\mathbf{2}]_t}$$

where $[S_\mathbf{1}]_0$ and $[S_\mathbf{2}]_0$ are initial concentrations, and $[S_\mathbf{1}]_t$ and $[S_\mathbf{2}]_t$ are concentrations at time *t* of both substrates. See Bunnett, J. F. *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part 1, p 159.

[20] The LUMO value of the C–Br σ^* MO in 1-BrAd (0.767 eV) is lower than the C–Br σ^* MO of 2-BrAd (0.867 eV). 1-ClAd (1.446 eV) has a C–Cl σ^* MO energy lower than the C–Cl σ^* MO of the 2-ClAd (1.548 eV). The calculations were carried out with the AM1 method.

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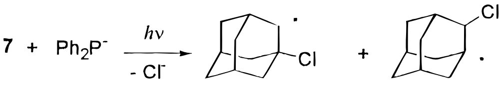
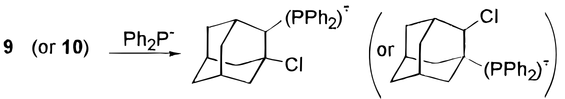
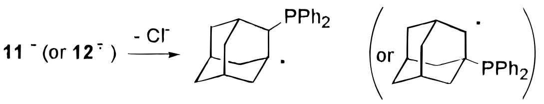
[22] A possibility for the formation of the reduction products is the ET from the nucleophile to the radical followed by protonation. However, although liquid ammonia is not a good hydrogen donor, radicals reacting poorly toward nucleophiles can be reduced by the solvent. As we do not have experimental evidence to favor one or the other mechanism we cannot state which of them occurs in our system.



9 **10** (8)



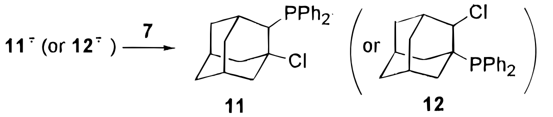
11·⁻ **12·⁻** (9)



13 **14** (10)

$$\mathbf{13}\ (\text{or } \mathbf{14}) \longrightarrow \underset{\mathbf{15}}{\text{2-AdPPh}_2}\ (\text{or } \underset{\mathbf{16}}{\text{1-AdPPh}_2}) \qquad (11)$$

The fact that no monosubstitution products **11** or **12** with retention of chlorine were found may indicate that the intermolecular ET to the substrate (eq 12) does not compete with the intramolecular ET to give radicals **13** and **14** (eq 10).



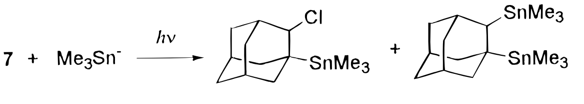
11 **12** (12)

+ **9** + **10**

Taking into account that the yield of **16** is four times higher than that of **15** it seems that when **7** receives an electron it fragments four times faster at the 1-position to give radical **10** than at the 2-position to give radical **9** (eq 8). On the other hand, 2-ClAd does not react with Ph_2P^- ions under irradiation, probably due to an inefficient photostimulated initiation step. However, the radical anion intermediate $\mathbf{12}^{-\bullet}$ has a fast intramolecular ET rendering finally the product observed.

In order to see if the lack of formation of the disubstitution product is due to the steric bulk of the radicals **13** and **14**, and that of the incoming nucleophile, we studied the reaction of **7** with a nucleophile with less steric bulk than Ph_2P^- ions. Estimation of the steric bulk of the trimethyltin group indicates that it is very similar to that of the chlorine and smaller than bromine groups.[23]

When **7** reacts under photostimulation with Me_3Sn^- ions mainly the monosubstitution product with retention of chlorine, (2-chloro-1-adamantyl)trimethyltin (**17**) (54%), and the disubstitution product, 1,2-bis(trimethystannyl) adamantane (**18**) (26%), were formed (eq 13). The reaction does not occur in the dark, and the photostimulated reaction is inhibited by *p*-DNB (Table 3, experiments 4−6).



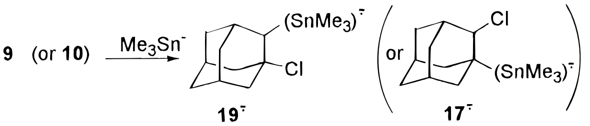
17 **18** (13)

The same relation of products **17** and **18** was found when the reaction was performed with a large excess of Me_3Sn^- ions and longer irradiation times (4 h), indicating that **17** is not an intermediate in the formation of **18**. Likewise, **17** fails to react with Me_3Sn^- ions in liquid ammonia (2 h irradiation, **18** < 4%) (Table 3, experiments 7 and 8).

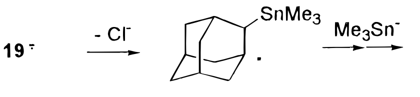
The fact that **17** does not react under irradiation with Me_3Sn^- ions but 2-ClAd does could be due to the well known powerful σ-electron donor capability of the Me_3-Sn group that would increase the LUMO energy of the C−Cl bond.

These results can be explained in terms of the $S_{RN}1$ mechanism. Under irradiation, **7** gives the radicals **9** and **10** in the sense of eq 8. The radicals **9** and **10** couple with the nucleophile to give the radical anions intermediates $\mathbf{17}^{-\bullet}$ and $\mathbf{19}^{-\bullet}$ (eq 14).

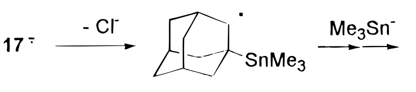
These radical anions intermediates show different behavior. The radical anion $\mathbf{19}^{-\bullet}$ gives only the intramolecular ET to form radical **20** and chloride ion. Radical **20** couples with the nucleophile to give ultimately the disubstitution product **18** (eq 15). The monosubstitution product with retention of chlorine formed by intermolecular ET is not observed. In contrast, the radical anion intermediate $\mathbf{17}^{-\bullet}$ has two competitive reactions, intramolecular ET to give radical **21**, which ultimately gives the disubstitution product **18** (eq 16), or intermolecular ET to give **17**, which is not an intermediate to form **18** (eq 17).



19·⁻ **17·⁻** (14)



20 (15)



21 (16)

$$\mathbf{17}^{\cdot-} \xrightarrow{\text{ET}} \mathbf{17} \overset{\text{Me}_3\text{Sn}^-}{\not\longrightarrow} \mathbf{18} \qquad (17)$$

If the rate of formation of radicals **9** and **10** by photostimulated intermolecular ET from the nucleophiles (Ph_2P^- or Me_3Sn^- ions) or by any radical anion intermediate is the same (**9**:**10** ≈ 15:64 determined by product analysis of the reaction with Ph_2P^- ions), the yield of **18** formed through eqs 14 and 15 should be ≈15%, and ≈11−15% formed through eqs 14 and 16 in order to account for the ≈26−30% yield of **18**.

As the substitution product **17** did not give **18**, the ratio of the competing reactions of radical anion $\mathbf{17}^{-\cdot}$, the intramolecular ET to give **18** (eq 16, ≈11−15%) and the intermolecular ET to give **17** (eq 17, ≈50−54%), is approximately 4, on the basis of product analysis.

Conclusions

These results show that 2-ClAd does not react under irradiation with Ph_2P^- ions, but Me_3Sn^- does, giving good yields of the substitution product, which indicates that Me_3Sn^- ions are more reactive in the initiation step of the $S_{RN}1$ mechanism. A more reactive substrate, such as 2-BrAd, reacts with Ph_2P^- ions under irradiation.

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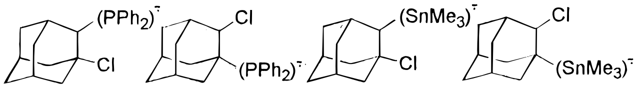
[23] Davis, D. D.; Surmatis, A. J.; Robertson, G. L. *J. Organomet. Chem.* **1972**, *46*, C9.

By competition experiments with Me_3Sn^- ions, 1-ClAd is 12 times more reactive than 2−ClAd, and by competition experiments with Ph_2P^- ions or Me_3Sn^- ions, 1-BrAd is 1.4 times more reactive than 2-BrAd, indicating that the 1-position is more reactive than the 2-position, and this difference is higher with the poorest leaving group.

When **7** receives an electron, two positions are reactive, but the fragmentation rate at the 1-position is *ca.* 4 times faster than at the 2-position, as suggested in the reactions with Ph_2P^- ions. The radicals formed by intramolecular ET do not couple with the nucleophile probably due to the steric bulk of both the nucleophile Ph_2P^- and the diphenylphosphinyl moiety of the radical intermediates, thus only the monosubstitution products are formed.

In the reaction of **7** with Me_3Sn^- ions, a less sterically bulky nucleophile, the disubstitution product is obtained, together with the monosubstitution product with retention of chlorine **17**. It is interesting to note that similar radical anions have different rates in ET reactions; thus the intramolecular ET of the radical anions $\mathbf{11}^{-\bullet}$, $\mathbf{12}^{-\bullet}$, and $\mathbf{19}^{-\bullet}$ to the C−Cl bond is much faster than the intermolecular ET, and none of the monosubstitution products with retention of chlorine are obtained. However, in the radical anion $\mathbf{17}^{-\bullet}$, the intermolecular ET is *ca.* 4 times faster than the intramolecular ET under our experimental conditions.[24]



$\mathbf{11}^{-\bullet}$ $\mathbf{12}^{-\bullet}$ $\mathbf{19}^{-\bullet}$ $\mathbf{17}^{-\bullet}$

Experimental Section

General Methods. Irradiation was conducted in a reactor equipped with two 250-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water-refrigerated). Column chromatography was performed on silica gel (70−270 mesh ASTM).

Materials. Reagents 2-ClAd (98%, Johnson Matthey-Alfa Products), 1-BrAd, 1-ClAd, and 2-BrAd (98%, Aldrich), 1-hydroxyadamantane (Sigma), and *p*-DNB (Fluka) were used as received. Ph_2P^- ions were prepared from Ph_3P (Fluka) and Na metal in liquid ammonia. Me_3Sn^- ions were prepared from Me_3SnCl (Fluka) and Na metal in liquid ammonia.[25]

Synthesis of Reactants. 4-Protoadamantanone was prepared from 1-hydroxyadamantane as described[26] by rearrangement of bridgehead alcohol and then purified by chromatography on aluminum oxide (6% w/w) and eluted with petroleum ether: mp 201−2 °C (lit[26] mp 202−204 °C). The IR[26] and ^{1}H NMR[27] are identical to those reported. Synthesis of 1,2-dichloroadamantane: The reaction between 4-protoadamantanone and $HCl/ZnCl_2$ was carried out as described.[28] The 1,2-dichloroadamantane was isolated as a white solid after chromatography on silica gel and eluted with petroleum ether: mp 186−188 °C (lit[28] mp 186−7 °C).

Photostimulated Reaction of 2-BrAd with Ph_2P^- Ions in Liquid Ammonia. The following procedure is representative of all the reactions. Into a three-necked, 500-mL, round-bottomed flask equipped with a cold finger condenser charged with dry ice−ethanol, a nitrogen inlet, and a magnetic stirrer were condensed 300 mL of ammonia previously dried with Na metal under nitrogen. Ph_3P (1 mmol) and Na metal (2 mmol) were added to form Ph_2P^- ions, and *t*-BuOH (1 mmol) was added to neutralize the amide ions formed. To this solution was added 1 mmol of substrate and then irradiated for 1 h. The reaction was quenched by adding NH_4NO_3 in excess, and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with diethyl ether and with methylene chloride, too. The products were oxidized with H_2O_2 and then quantified by GLC using the internal standard method. In another experiment the product was oxidized with H_2O_2, and **2** was isolated as a white solid after chromatography on silica gel, eluted with diethyl ether, and recrystallized from benzene: mp 209−210 °C (lit[21] mp 209−211 °C).

Photostimulated Reaction of 1,2-Dichloroadamantane with Ph_2P^- Ions in Liquid Ammonia. The procedure was similar to that for the previous reaction, except that 1,2-dichloroadamantane was used as substrate. In this case the reaction was irradiated for 4 h. The products were oxidized and then quantified by GLC with the internal standard method. The products **2**[21] and **8**[29] were compared with authentic samples.

Photostimulated Reaction of 1-ClAd with Me_3Sn^- Ions in Liquid Ammonia. The following procedure is representative of these reactions. The equipment used has been described for the reaction with Ph_2P^- ions. Nucleophile Me_3Sn^- was prepared in liquid ammonia (lemon yellow solution) from Me_3SnCl (0.5 mmol) and Na metal (1.2 mmol, 20% excess). The 1-ClAd (0.5 mmol dissolved in 1 mL of anhydrous diethyl ether) was added, and then irradiated for 20 min. The procedure was as usual. After workup, 1-(trimethylstannyl)-adamantane[14,30,31] was purified by sublimation (liquid air cooling, 52−3 °C) to afford white crystals: mp 56−7 °C (lit.[14,30] mp 56−7 °C). ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9 H, $SnMe_3$; J_{Sn-H} 47.57 and 49.81 Hz); 1.75−2.20 (m, 15 H).

Photostimulated Reaction of 2-ClAd with Me_3Sn^- Ions in Liquid Ammonia. Under the conditions described above, 2-(trimethylstannyl)adamantane was formed after 75 min of irradiation and isolated as white crystals by column chromatography with light petroleum ether on silica gel: mp 37−8 °C (lit.[30,31] mp 37−8 °C). ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $SnMe_3$; J_{Sn-H} 47.60 and 50.00 Hz); 1.65−2.08 (m, 15 H).

Photostimulated Reaction of 1,2-Dichloroadamantane with Me_3Sn^- Ions in Liquid Ammonia. Using the procedure described above, 1,2-dichloroadamantane (0.5 mmol) was allowed to react with Me_3Sn^- ions (1 mmol). The residue was column chromatographed on silica gel and eluted with light petroleum ether. **1,2-Bis(trimethylstannyl)adamantane:** It was isolated as a white solid and carefully sublimed (38−42 °C) and recrystallized from acetone keeping it in a freezer: mp 52−3 °C. ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H, $SnMe_3$) and 0.10 (s, 9 H), J_{Sn-H} not obsd; 1.68−2.27 (m, 14 H). ^{13}C NMR ($CDCl_3$) δ −11.06 (J_{C-Sn} 271.88 and 284.72 Hz), −7.30 (J_{C-Sn} 278.32 and 291.29 Hz), 29.18 (J_{C-Sn} 50.30 Hz), 29.25 (J_{C-Sn} 47.91 Hz), 29.71 (J_{C-Sn} not obsd), 33.31 (J_{C-Sn} 55.36 Hz), 36.84 (12.82 Hz), 38.25 (J_{C-Sn} 6.58 Hz), 40.45 (J_{C-Sn} 8.69 Hz), 40.63, 45.66 (J_{C-Sn} 69.54 Hz), 45.74 (J_{C-Sn} 400.27 and 418.87 Hz). Mass spectra similar to report.[27] Anal. Calcd for $C_{16}H_{32}Sn_2$: C 41.61, H 6.98. Found: C 41.52, H 7.07. **2-Chloro-1-(trimethylstannyl)adamantane:** a solid purified by sublimation: mp 65.5−66.5 °C. ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, J_{Sn-H} 47.6 and 51.4 Hz); 1.60−2.51 (m, 13 H); 4.60 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ −11.08 (J_{C-Sn} 297.80 and 313.00 Hz), 27.38 (J_{C-Sn} 42.15 Hz), 28.30 (J_{C-Sn} 42.89 Hz), 31.15, 35.22 (J_{C-Sn} 7.40 Hz), 36.36, 36.73 (J_{C-Sn} 29.94 Hz), 37.85 (J_{C-Sn} 6.54 Hz), 38.44, 42.74 (J_{C-Sn} 13.18 Hz), 75.39 ppm (J_{C-Sn} 23.65 Hz). MS: *m/z* (rel intensity) M^+ not obsd 41 (7.6), 57 (21.6), 79 (23.4), 91 (31.02), 92 (100), 93 (28.4), 105 (18.8), 119 (18.1), 134 (82.0), 165 (3.74)

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(24) We tried to theoretically explain the difference in behavior between radical anions $\mathbf{17}^{-\bullet}$ and $\mathbf{19}^{-\bullet}$. However, PM3 calculations do not show an energy difference between the SOMO and the C−Cl σ^* MOs of both intermediates.

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135 (14.0), 185 (13.0). Anal. Calcd for $C_{13}H_{23}ClSn$: C 46.82, H 6.95, Cl 10.63. Found: C 46.83, H 7.00, Cl 10.87.

Reaction of Different Substrates with Ph_2P^- or Me_3Sn^- Ions in the Dark. The described procedure was followed, except that the reaction flask was wrapped with aluminum foil.

Inhibited Reaction of Different Substrates with Ph_2P^- or Me_3Sn^- Ions. The procedure was similar to that for the previous reaction, except that 20 mol % of *p*-DNB were added to the solution of nucleophile prior to substrate addition.

Competition Experiments. Relative reactivity of 1-ClAd vs 2-ClAd: The nucleophile was prepared in liquid ammonia as before from Me_3SnCl (0.5 mmol). Both substrates were dissolved in 1 mL of anhydrous diethyl ether, and after 75 min of irradiation the reaction was quenched with NH_4NO_3 in excess. The reaction mixture was extracted with diethyl ether and water. Substitution products were quantified by GLC with the internal method. Relative reactivity of 1-BrAd vs 2-BrAd: The nucleophiles (Ph_2P^- or Me_3Sn^-) were prepared in liquid ammonia, and the competition reactions were as carried out as before.

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