Reactions of Triorganostannyl Ions with Haloarenes in Liquid Ammonia. Competition between Halogen–Metal Exchange and Electron-Transfer Reactions

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Received April 3, 1992

The reactions between triorganostannyl ions and haloarenes in liquid ammonia can lead to substitution and to reduction products. It was found that, depending on the structure of the tin nucleophile, the halogens involved, the structure of the haloarene, and the experimental conditions, the reactions can follow exclusively either an $S_{RN}1$ mechanism (substitution products), or a halogen–metal exchange (HME) mechanism (dehalogenation–reduction products) and that a competition between both mechanisms (mixture of substitution and reduction products) is also possible. With triphenylstannyl ions (2) good yields of products of nucleophilic substitution ($S_{RN}1$ mechanism) were obtained when the reactions were carried out with chloroarenes (e.g., *p*-chlorotoluene, *p*-dichlorobenzene, 1-chloronaphthalene, and 2-chloroquinoline) and with some bromoarenes (e.g., *p*-bromotoluene); with iodoarenes only HME reaction products were obtained. With trimethylstannyl ions (17) only chloroarenes reacted through the $S_{RN}1$ mechanism. The relative reactivity of 2, 17, and diphenylphosphide ions toward *p*-anisyl radicals, obtained in competition experiments, is also reported.

The radical mechanism of aromatic nucleophilic substitution, or $S_{RN}1$, is a well-known process by which a substitution is produced on a nonactivated adequately substituted substrate.[3] The propagation steps are shown in Scheme I.

Scheme I

$$(RX)^{\bullet -} \rightarrow R^{\bullet} + X^{-} \quad (1)$$

$$R^{\bullet} + Nu^{-} \rightarrow (RNu)^{\bullet -} \quad (2)$$

$$(RNu)^{\bullet -} + RX \rightarrow (RX)^{\bullet -} + RNu \quad (3)$$

Overall, Scheme I depicts a nucleophilic substitution in which radicals and radical anions are intermediates. However, this chain process requires an initiation step. In a few systems, spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed, and the radical anion $(RX)^{\bullet -}$ that is formed initiates the chain propagation steps. When the ET reaction does not occur spontaneously, it can be induced by light stimulation.[3]

The number of examples of the aromatic $S_{RN}1$ reaction has expanded to include reactions of aromatic and heteroaromatic substrates with a variety of nucleophiles such as carbanions and nucleophiles derived from N, P, As, Sb, S, Se, and Te.[3]

Although the reaction of triorganostannyl ions as nucleophiles with haloarenes has long been known, there are few reports concerning the mechanism of these reactions, and contradictory results have been found according to the solvent or reaction conditions.

The reaction of trimethylstannylsodium (Me_3SnNa) with halobenzenes (chloro, bromo, and iodo) in liquid ammonia gives a very low yield of phenyltrimethyltin ($PhMe_3Sn$),[4] and it was reported that the reaction of *p*-dichlorobenzene with Me_3SnNa in liquid ammonia and diethyl ether as cosolvent gives the disubstitution product without indication of the mechanism or the yield.[5]

The reaction of triphenylstannyl sodium (Ph_3SnNa) and haloarenes does not give substitution products in liquid ammonia, and dehalogenation is the main reaction.[6] In a later report the reaction of bromobenzene with Me_3SnNa in liquid ammonia was described,[7] leading to benzene as main product (96% yield) together with some phenyltrimethyltin ($PhMe_3Sn$) (4% yield), i.e., the substitution product. The reaction of Me_3SnNa with halobenzenes (chloro, bromo, and iodo) in tetraglyme gives Me_3SnPh and also variable amounts of benzene, diphenyldimethyltin (Ph_2Me_2Sn), and tetramethyltin (Me_4Sn) (eq 4).[7]

$$PhX + Me_3SnNa \rightarrow PhH + Me_3SnPh + Me_2SnPh_2 + Me_4Sn \quad (4)$$

From trapping experiments of carbanions with *tert*-butyl alcohol and solvent effects, it was proposed that the reaction occurred by a halogen–metal exchange (HME) in a solvent cage. The formation of the subproducts Me_2SnPh_2 and Me_4Sn has been ascribed to the decomposition of Me_3SnNa into MeNa and dimethylstannylene (Me_2Sn).[7]

Further evidences of the HME mechanism were found in the reaction of Me_3SnNa with *o*-dibromobenzene. The disubstitution product *o*-bis(trimethylstannyl)benzene was obtained in 42% yield, but part of the intermediate *o*-bromophenyl anion decomposes into benzyne which is then trapped with furan to give the corresponding Diels–Alder adduct.[8]

The reaction of *o*-, *m*-, and *p*-bromotoluenes with tributylstannyllithium (Bu_3SnLi) in THF gave the straightforward substitution product. However, cine substitution products were found with *p*-chloro and *p*-fluorotoluenes, indicating that a benzyne mechanism operates. The relationship of the products depends on whether the reactions were carried out in the dark or under irradiation or in the presence of added substances. When radical traps were added, more cine substitution products were found, and in the presence of Li metal, the yield of the ipso substitution products increased. These results suggest that the reaction, at least partly, occurs by a radical mechanism.[9]

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(3) For reviews, see: (a) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the SRN1 Mechanism*; ACS Monograph 178; Washington, D.C., 1983. (b) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283.

(4) Bullard, R. H.; Robinson, W. B. *J. Am. Chem. Soc.* **1927**, *49*, 1368.

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(6) Chambers, R. F.; Scherer, P. C. *J. Am. Chem. Soc.* **1926**, *48*, 1054.

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(8) Kuivila, H. G.; Wursthorn, K. R. *J. Organomet. Chem.* **1976**, *105*, C6. Wursthorn, K. R.; Kuivila, H. G. *J. Organomet. Chem.* **1977**, *140*, 29.

0022-3263/92/1957-5720$03.00/0

Table I. Reaction of Triphenylstannyl Ions 2 with Haloarenes in Liquid Ammonia[a]

expt	ArX[b] (M 10^3)	**2** (M 10^3)	condn (min)	X^- (%)	substn products (% yield)[c]
1	*p*-ClTo (1.2)	2.1	dark (60)	≤5	*p*-$ToPh_3Sn$ (0)
2	*p*-ClTo (2.4)	3.2	$h\nu$ (60)	67	*p*-$ToPh_3Sn$ (58)
3	*p*-ClTo (6.4)	3.2	$h\nu$ (120)	*d*	*p*-$ToPh_3Sn$ (75)
4	*p*-ClTo (2.8)	2.8	$h\nu$ (60)[e]	≤5	*p*-$ToPh_3Sn$ (0)
5	*p*-BrTo (2.8)	2.8	dark (60)	≤5	*p*-$ToPh_3Sn$ (4)
6	*p*-BrTo (2.8)	2.8	$h\nu$ (60)	81	*p*-$ToPh_3Sn$ (62)
7	*p*-BrTo (2.8)	2.8	$h\nu$ (60)[e]	49	*p*-$ToPh_3Sn$ (33)
8	*p*-ITo (2.8)	2.8	dark (60)	60	*p*-$ToPh_3Sn$ (0)[f]
9	*p*-ITo (2.8)	2.8	$h\nu$ (60)	*d*	*p*-$ToPh_3Sn$ (38)[f]
10	*p*-IAn (4.0)	4.0	dark (90)	80	*p*-$AnPh_3Sn$ (0)[f]
11	*p*-IAn (2.8)	2.8	$h\nu$ (60)	*d*	*p*-$AnPh_3Sn$ (20)[f]
12	*p*-$Cl_2C_6H_4$ (2.8)	6.4	dark (60)	≤5[g]	*p*-$(Ph_3Sn)_2C_6H_4$ (0)
13	*p*-$Cl_2C_6H_4$ (2.8)	5.6	$h\nu$ (60)	54[g]	*p*-$(Ph_3Sn)_2C_6H_4$ (51)[h]
14	*p*-$Cl_2C_6H_4$ (2.8)	6.0	$h\nu$ (180)	87[g]	*p*-$(Ph_3Sn)_2C_6H_4$ (69)[h]
15	*p*-$Br_2C_6H_4$ (2.8)	6.0	dark (60)	44[g]	*p*-$(Ph_3Sn)_2C_6H_4$ (0)[i]
16	*p*-$Br_2C_6H_4$ (2.8)	5.6	$h\nu$ (60)	88[g]	*p*-$(Ph_3Sn)_2C_6H_4$ (22)[h,j]
17	1-ClNaph (2.8)	3.2	dark (180)	9	1-$NaphPh_3Sn$ (6)[h]
18	1-ClNaph (2.8)	3.2	$h\nu$ (180)	86	1-$NaphPh_3Sn$ (80)[h,k]
19	1-BrNaph (2.8)	3.2	dark (60)	40	1-$NaphPh_3Sn$ (<5)[h,l]
20	1-BrNaph (8.0)	4.4	$h\nu$ (60)	100	1-$NaphPh_3Sn$ (75)[h,m]
21	2-ClQuin (2.8)	3.2	dark (60)	≤5	2-$QuinPh_3Sn$ (0)
22	2-ClQuin (2.8)	3.2	$h\nu$ (60)	87	2-$QuinPh_3Sn$ (80)[h]

[a] Reactions carried out in ca. 250 mL of liquid ammonia. [b] To = tolyl; An = anisyl (*p*-methoxyphenyl); Naph = naphthyl; Quin = quinolyl. [c] Determined by NMR unless otherwise indicated. [d] Not quantified. [e] *p*-Dinitrobenzene was added (11 mol %). [f] Ph_3SnI was detected as product, together with Ph_3SnOH and $(Ph_3Sn)_2O$. [g] The indicated yield was obtained considering two halogens per mole of substrate. [h] Isolated yield. [i] Bromobenzene was formed in 96% yield (GLC). [j] Tetraphenyltin was formed in 40% yield (isolated yield). [k] Naphthalene was formed in 9% yield (GLC). [l] Naphthalene was formed in 32% yield (GLC). [m] Naphthalene was formed in 24% yield (GLC).

The fact that aromatic radicals have been shown to react quite efficiently with different organometallic nucleophiles by the $S_{RN}1$ mechanism,[3] and that the reaction of triorganostannyl ions with haloarenes has not been studied systematically in liquid ammonia as solvent, prompted us to study the photostimulated reaction between haloarenes and triorganostannyl ions in this solvent. These studies can be of interest not only from a mechanistic point of view but also as a synthetic route to organotin compounds with mixed organic ligands.

Results and Discussion

Reaction of Ph_3SnNa (2) with Haloarenes in Liquid Ammonia. The nucleophile **2** was prepared either from reaction of triphenyltin chloride **1a** (eq 5a) or hexaphenylditin **1b** (eq 5b) with Na metal in liquid ammonia.

$$\underset{\mathbf{1a}}{Ph_3SnCl} + 2Na \rightarrow \underset{\mathbf{2}}{Ph_3Sn^-} + Cl^- + 2Na^+ \qquad (5a)$$

$$\underset{\mathbf{1b}}{(Ph_3Sn)_2} + 2Na \rightarrow \underset{\mathbf{2}}{2Ph_3Sn^-} + 2Na^+ \qquad (5b)$$

A series of halotoluenes reacted with **2** (Table I). *p*-Chloro (**3a**) and *p*-bromotoluene (**3b**) showed typical $S_{RN}1$ behavior; they were unreactive in the dark, but could be photostimulated to react rapidly to give the product **4a** (eq 6).

$$ArX + \mathbf{2} \xrightarrow{h\nu} ArSnPh_3 + X^- \qquad (6)$$

3a: *p*-$ClC_6H_4CH_3$
3b: *p*-$BrC_6H_4CH_3$
3c: *p*-$IC_6H_4CH_3$
3d: 1–chloronaphthalene
3e: 1–bromonaphthalene
3f: 2–chloroquinoline

4a: Ar = *p*-$CH_3C_6H_4$
4b: Ar = 1–naphthyl
4c: Ar = 2–quinolyl

The fact that **3a** and **3b** do not react in the dark but under irradiation, and that the photostimulated reactions were inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions,[3] strongly suggests that **3a** and **3b** react with **2** by the $S_{RN}1$ mechanism.

In contrast, the reaction of *p*-iodotoluene (**3c**) with **2** in the dark did not give product **4a** after 60 min, although a 60% yield of iodide ions was detected together with toluene, triphenyltin hydroxide (Ph_3SnOH), and bis(triphenyltin) oxide [$(Ph_3Sn)_2O$]. In another reaction under the same experimental conditions but without adding water in the workup, it was possible to isolate a small amount of triphenyltin iodide (Ph_3SnI) as product (Table I, experiment 8). In an independent experiment Ph_3SnI and amide ions afforded the same product mixture after the usual workup.

These results suggest that the reaction of **3c** with **2** occurs by an HME mechanism, giving *p*-tolylsodium (**5**) and Ph_3SnI. The intermediate anion **5** is protonated by ammonia giving toluene (**6**) as product (eq 7).

$$\underset{\mathbf{3c}}{p\text{-}IC_6H_4CH_3} + \mathbf{2} \xrightarrow{-Ph_3SnI} \underset{\mathbf{5}}{p\text{-}CH_3C_6H_4^-} \xrightarrow{NH_3} \underset{\mathbf{6}}{C_6H_5CH_3} \qquad (7)$$

The fact that **4a** was not found clearly indicates that **5** and Ph_3SnI do not react to give **4a** in liquid ammonia.

In order to know if the $S_{RN}1$ mechanism can compete with the reaction of HME, we carried out the same reaction under irradiation but only a 38% yield of **4a** was found (Table I, experiment 9). This result indicates a very fast HME reaction taking into account that, in photostimulated reactions, iodoarenes react faster than the bromo or chloro derivatives.[3]

The same results were found with *p*-iodoanisole as substrate, i.e., a very fast HME occurred with **2**, and the photostimulated reaction did not compete with the HME reaction (Table I, experiments 10–11).

When the substrate is *p*-dichlorobenzene (**7**) there is no reaction with **2** in liquid ammonia in the dark, but under irradiation the disubstitution product **11** was obtained in high yields (Table I, experiments 12–14).

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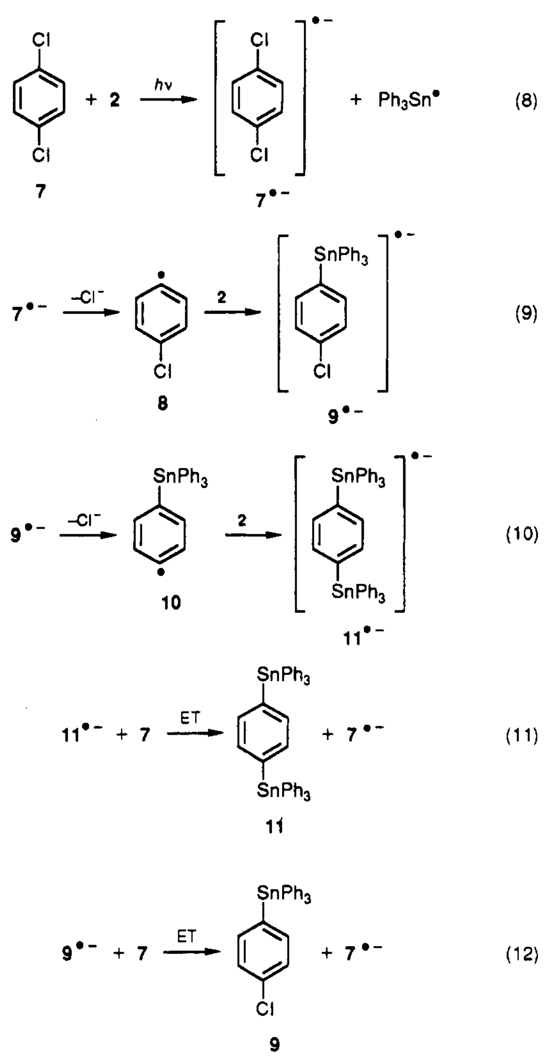
(9) Quintard, J. P.; Hauvette-Frey, S.; Pereyre, M. *J. Organomet. Chem.* **1976**, *112*, C11; **1978**, 159, 147.

Scheme II



These results suggest that this reaction also occurs by the $S_{RN}1$ mechanism, as sketched in Scheme II.

Once substrate **7** receives as electron from **2**, under irradiation, the former forms $7^{\bullet-}$ (eq 8). Radical anion $7^{\bullet-}$ fragments to give *p*-chlorophenyl radical **8**, which then couples with **2** to form the radical anion $9^{\bullet-}$ (eq 9). $9^{\bullet-}$ fragments to give the radical **10**, which couples with **2** leading to a new radical anion $11^{\bullet-}$ (eq 10), which by an ET process to **7** gives both the disubstitution product **11** and $7^{\bullet-}$ (eq 11) to follow the chain propagation cycle of this mechanism.

The fact that monosubstitution product *p*-chlorophenyltriphenyltin (**9**) was not found in these reactions suggests that the fragmentation reaction of $9^{\bullet-}$ (eq 10) is much faster than the ET to **7** (eq 12).

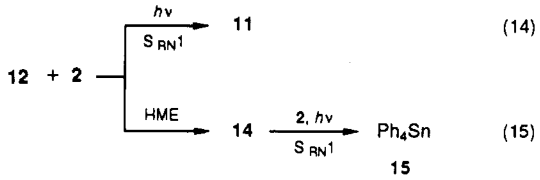
In the photostimulated reaction (60 min), both substrate **7** and disubstitution product **11** were found in similar yields, but **9** was not present at all. If **9** were an intermediate, it would accumulate during the reaction because **7** should be more reactive than **9** in ET reactions. The behavior of dihaloarenes with nucleophiles in $S_{RN}1$ reactions is well-known as well as the partitioning between mono- and disubstitution products.[3,10]

On the other hand, the reaction of *p*-dibromobenzene (**12**) with **2** in the dark gave bromobenzene (**14**) as the only product (96% yield, Table I, experiment 15). This result indicates a fast HME reaction and that the intermediate anion **13** is being protonated by the ammonia to give **14**, which does not react by an HME reaction with **2** (eq 13).

$$\underset{12}{p\text{-}Br_2C_6H_4} + 2 \xrightarrow{-Ph_3SnBr} \underset{13}{p\text{-}BrC_6H_4^-} \xrightarrow{NH_3} \underset{14}{C_6H_5Br} \quad (13)$$

To know if the ET process can compete with the HME mechanism, we studied the photostimulated reaction of **12** with **2** under the best conditions for the $S_{RN}1$ mechanism, that is, the addition of **12** to a solution of **2** under irradiation. The reaction products were **11** (22% yield) and tetraphenyltin (**15**) (40% yield).

This result clearly indicates a competition between ET ($S_{RN}1$, eq 14) and the HME mechanisms. The latter gives **14** as intermediate which, under irradiation, reacts wtih **2** through the $S_{RN}1$ mechanism to give **15** as product (Table I, experiment 16) (eq 15).



1-Chloronaphthalene (**3d**) reacts in the dark very slowly with **2**. Thus, it gives 6% yield of 1-naphthyltriphenyltin (**4b**). However, under irradiation **4b** was isolated in an 80% yield (Table I, experiment 17 and 18). These results suggest that in the dark **3d** reacts slowly with **2** by an HME reaction or by a spontaneous (thermal) ET process which initiates the $S_{RN}1$ reaction,[11] whereas under irradiation the reaction proceeds much faster to give mostly the product **4b**, showing that in the competition between both mechanisms the ET process is faster in this case than the HME reaction.

On the other hand, 1-bromonaphthalene (**3e**) reacts with **2** in the dark to give bromide ions (40%), a very low yield of the product **4b** (≤5%), and naphthalene as main product (32%), indicating that the HME reaction operates with this substrate. However, under irradiation the reaction was complete, and **4b** was obtained in a 76% yield (Table I, experiments 19 and 20), indicating that the ET process is quite fast under these experimental conditions and that it is able to compete efficiently with the HME reaction.

2-Chloroquinoline (**3f**) does not react in the dark with **2**, but under irradiation it gives the substitution product 2-quinolyltriphenyltin (**4c**) in high yields (Table I, experiments 21 and 22).

Reaction of Me_3SnNa (17) with Haloarenes in Liquid Ammonia. In order to determine the effect of the structure of the triorganostannyl ions on the reactivity with haloarenes, i.e. whether the HME and the $S_{RN}1$ mechanism would be favored, we studied the reactions of nucleophile **17** with different substrates in liquid ammonia. The nucleophile **17** was prepared in liquid ammonia through the reaction of trimethyltin chloride with sodium metal.

p-Chloroanisole (**16a**) did not react with **17** in the dark (60 min), but under irradiation the substitution product **18a** was obtained in a very high yield (ca. 100%). The

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(10) Bunnett, J. F.; Traber, R. P. *J. Org. Chem.* **1978**, *43*, 1867. Bunnett, J. F.; Shafer, S. J. *J. Org. Chem.* **1978**, *43*, 1873, 1877. Carver, D. R.; Greenwood, T. D.; Hubbard, J. S.; Komin, A. P.; Sachdeva, Y. P.; Wolfe, J. F. *J. Org. Chem.* **1983**, *48*, 1180. Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164. Amatore, C.; Beugelmans, R.; Bois-Choussy, M. Combellas, C.; Thiebaults, A. *J. Org. Chem.* **1989**, *54*, 5688.

(11) We used Na metal to prepare the nucleophiles, and one possibility for the dark reaction may be that some of the metal was left and catalyzed the reaction, but this is not the case because we added the substrate to the light yellow solution of the nucleophile when all the solvated electrons (dark blue solution) reacted.

Table II. Reaction of Trimethylstannyl Ions 17 with Haloarenes in Liquid Ammonia[a]

expt	ArX[b] (M 10^3)	17 (M 10^3)	condn (min)	X$^-$ (%)	substn products (% yield)[c]
1	*p*-ClAn (6.0)	6.4	dark (60)	0	*p*-AnMe$_3$Sn (0)
2	*p*-ClAn (12.8)	14.0	*hν* (60)	100	*p*-AnMe$_3$Sn (100)
3	*p*-ClAn (4.0)	4.4	*hν* (60)[d]	0	*p*-AnMe$_3$Sn (0)
4	*p*-BrAn (12.8)	14.0	dark (5)	100	*p*-AnMe$_3$Sn (0)[e]
5	1-ClNaph (4.0)	4.4	dark (60)	4	1-NaphMe$_3$Sn (0)
6	1-ClNaph (12.0)	12.8	*hν* (60)	100	1-NaphMe$_3$Sn (90)
7	*p*-Cl$_2$C$_6$H$_4$ (4.0)	4.4	dark (60)[f]	12	*p*-(Me$_3$Sn)$_2$C$_6$H$_4$ (11)
8	*p*-Cl$_2$C$_6$H$_4$ (4.0)	8.8	*hν* (60)[f]	100	*p*-(Me$_3$Sn)$_2$C$_6$H$_4$ (88)
9	2-ClQuin (4.0)	4.4	dark (60)	74	2-QuinMe$_3$Sn (65)
10	2-ClQuin (4.0)	4.4	*hν* (60)	100	2-QuinMe$_3$Sn (96)
11	2-ClQuin (4.0)	4.4	dark (60)[d]	21	2-QuinMe$_3$Sn (12)

[a] Reactions carried out in ca. 250 mL of liquid ammonia. [b] An = anisyl (*p*-methoxyphenyl); Naph = naphthyl; Quin = quinolyl. [c] Determined by GLC. [d] *p*-Dinitrobenzene was added (20 mol %). [e] Anisole (97% yield, GLC) was found as product. [f] The yield indicated considers two halogens per mole of substrate.

photostimulated reaction was completely inhibited by *p*-DNB. These results indicate that **16a** reacts with **17** by the S$_{RN}$1 mechanism (Table II, experiments 1–3) (eq 16).

$$\mathrm{ArCl} + \mathrm{Me_3Sn^-} \xrightarrow{h\nu} \mathrm{ArSnMe_3} + \mathrm{Cl^-} \qquad (16)$$

16a: *p*-MeOC$_6$H$_4$ 17
16b: 1-naphthyl
16c: 2-quinolyl

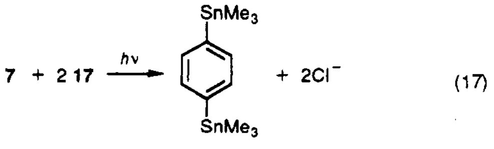
18a: Ar = *p*-MeOC$_6$H$_4$
18b: Ar = 1-naphthyl
18c: Ar = 2-quinolyl

On the other hand, *p*-bromoanisole reacts with **17** in less than 5 min, giving 100% of bromide ions and no substitution product **18b**, thus suggesting a very fast HME reaction with this substrate (Table II, experiment 4).

The reaction of 1-chloronaphthalene (**16b**) with **17** in the dark gave a 4% yield of chloride ions after 60 min, but no substitution product **18b** was found (Table II, experiment 5). However, after 60 min of irradiation a 100% yield of chloride ions was detected and (1-naphthyl)trimethyltin (**18b**) was obtained in a 90% yield (Table II, experiment 6).

There is a fast reaction in the dark between 2-chloroquinoline (**16c**) and **17**. A 65% yield of **18c** was obtained after 60 min. This reaction is light catalyzed and in the dark is partially inhibited by *p*-DNB (Table II, experiments 9–11). All these results suggest that there is a spontaneous (thermal) ET from **17** to **16c**, which is partially inhibited by *p*-DNB and accelerated by light.

The reaction between *p*-dichlorobenzene (**7**) and **17** in the dark is very slow and yields only an 11% of the disubstitution product **19** after 60 min. Under irradiation and after the same period of time, an 88% yield of **19** was obtained (Table II, experiments 7 and 8) (eq 17).



19

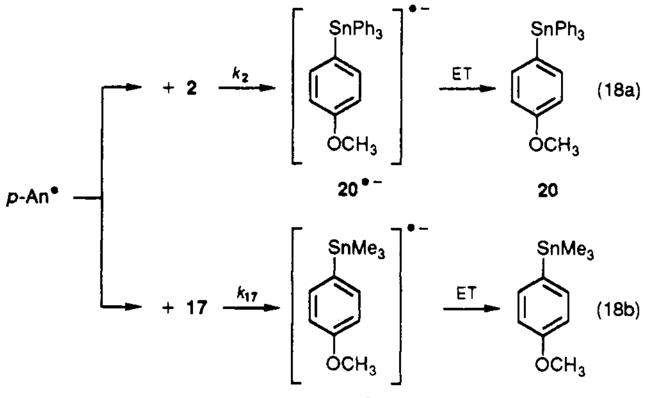
The fact that in the dark the only product observed is the disubstitution compound **19**, and that neither the monosubstitution product, (*p*-chlorophenyl)trimethyltin, nor the reduction product, chlorobenzene, were found, strongly suggests that there is a slow ET in dark reaction conditions and that the light catalyzes this reaction quite efficiently.

Table III. Competition Experiments between 2, 17, and Diphenylphosphide Ions vs *p*-Anisyl Radicals in Liquid Ammonia[a]

expt	Nu$_1^-$ (M 10^3)	Nu$_2^-$ (M 10^3)	*p*-ClAn[b] (M 10^3)	yield (%) product–Nu$_1$[c]	yield (%) product–Nu$_2$[d]
1	**2** (8.0)	**17** (8.0)	4.0	49[e]	43[f]
		rel reactivity k_2/k_{17} ca 1.1			
2	**17** (8.0)	Ph$_2$P$^-$ (8.0)	4.0	48[e]	44[g]
		rel reactivity $k_{17}/k_{\mathrm{Ph_2P^-}}$ ca 1.1			

[a] Reactions carried out in ca. 250 mL of liquid ammonia, with irradiation time of 60 min. [b] An = anisyl. [c] Substitution product from Nu$_1^-$. [d] Substitution product from Nu$_2^-$. [e] Determined by GLC. [f] Isolated yield. [g] Quantified as *p*-anisyldiphenylphosphine oxide (isolated yield).

Competition Experiments. All the reactions studied indicate, qualitatively, that **17** is more reactive than **2** in S$_{RN}$1 reactions (compare, for instance, experiments 13 and 18 in Table I with experiments 8 and 6 in Table II). As the S$_{RN}$1 mechanism is a chain reaction that needs an initiation step which is then followed by the propagation steps (Scheme I), we decided to study the relative reactivity of both nucleophiles in the *propagation* step, that is, the coupling of an aromatic radical with the nucleophile (Scheme I, eq 2). We studied the relative reactivity of **2** (eq 18a) vs **17** (eq 18b) towards *p*-anisyl radicals (*p*-An•) in liquid ammonia.



20•− **20**

18a•− **18a**

Once the yields of *p*-anisyltriphenyltin **20** and *p*-anisyltrimethyltin **18a** were determined in the photostimulated reaction of *p*-chloroanisole **16a** with **2** and **17** in excess, it is possible to calculate k_2/k_{17} by using eq 19,[12]

$$\frac{k_2}{k_{17}} = \frac{\ln [2]_0/[2]_t}{\ln [17]_0/[17]_t} \qquad (19)$$

where $[2]_0$ and $[17]_0$ are initial concentrations and $[2]_t$ and $[17]_t$ are concentrations at time *t*. This equation is based on a first-order reaction of both nucleophiles with *p*-anisyl radicals.

We found that both nucleophiles have almost the same relative reactivity toward *p*-anisyl radicals (Table III, experiment 1). This indicates that they have the same reactivity in the coupling reaction with *p*-anisyl radicals in *competition* experiments; in *separated* experiments **17** is more reactive than **2**. These results suggest that **17** should be more reactive than **2** in the photostimulated ET of the initiation step.[13]

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[12] Bunnett, J. F. *Investigation of Rates and Mechanism of Reactions*, 3rd ed.; Lewis, E. S., Ed.; Wiley Interscience: New York, 1074; Part I, p 159.

The reactivity of different nucleophiles toward aryl radicals has been studied, and it has been found that diphenylphosphide ions (Ph_2P^-) are among the most reactive toward these radicals. It was suggested that Ph_2P^- ions react at the diffusion-controlled rate.[14]

In order to compare the relative reactivity of triorganyltin nucleophiles, we determined the relative reactivity of **17** vs Ph_2P^- ions toward *p*-anisyl radicals with the same method as before, and we found that both have almost the same relative reactivity (Table III, experiment 2). This result indicates that nucleophiles **2** and **17** and Ph_2P^- ions react at the same rate with *p*-anisyl radicals and probably at the diffusion-controlled rate.

Conclusions. The reaction of triorganylstannyl ions with haloarenes in liquid ammonia may depend on the structure of the tin nucleophile, the halogens involved, the structure of the aromatic substrates and whether the latter are mono- or dihalosubstituted, and on the experimental conditions (whether the reactions are carried out in the dark or under irradiation). Depending on these variables, the reactions may follow exclusively either an $S_{RN}1$ mechanism (substitution products) or an HME mechanism (dehalogenation products), and also a competition between both mechanisms is possible.

Thus, whereas nucleophile **2** does not react in the dark with *p*-chloro- and *p*-bromotoluenes, *p*-dichlorobenzene, 1-chloronaphthalene, and 2-chloroquinoline, showing that there is no HME reaction, good yields of substitution products were obtained ($S_{RN}1$) under irradiation. When iodide (*p*-iodotoluene and *p*-iodoanisole) and bromide (*p*-dibromobenzene and 1-bromonaphthalene) are the leaving groups, there was a fast HME reaction and the intermediate carbanions were protonated by the liquid ammonia giving the dehalogenation products.

It is noteworthy that in the case of *p*-dibromobenzene the HME reaction leads to bromobenzene which does not undergo an HME process, and under irradiation it reacts by the $S_{RN}1$ mechanism as shown by the formation of tetraphenyltin. Although 1-bromonaphthalene reacts in the dark through an HME mechanism, this reaction is relatively slow and under irradiation it reacts mainly by an $S_{RN}1$ mechanism (76% yield of substitution product).

With **17** only compounds that have chlorine as leaving group like *p*-chloroanisole, 1-chloronaphthalene, *p*-dichlorobenzene, and 2-chloroquinoline do not react by an HME mechanism. These compounds react by the $S_{RN}1$ mechanism to give almost quantitative yields of substitution products. 2-Chloroquinoline reacts in the dark, indicating a spontaneous ET process from **17** to the substrate; this dark reaction is partially inhibited by *p*-DNB. *p*-Bromoanisole and probably all the aryl bromides and iodides react by an HME mechanism.

These results strongly suggest that using nucleophile **2** it is possible to obtain products of nucleophilic substitution by the $S_{RN}1$ mechanism with chloroarenes and with some bromoarenes, whereas with iodoarenes only products of the HME reaction are obtained. Using the nucleophile **17** only chloroarenes react through the $S_{RN}1$ mechanism.

By competition experiments, we found that both nucleophiles **2** and **17** react at the same rate as Ph_2P^- ions with *p*-anisyl radicals in liquid ammonia, and probably at the diffusion-controlled rate. However, **17** is more reactive than **2** in overall reactivity, probably because **17** is more reactive in the initiation step of the $S_{RN}1$ mechanism.[13]

Experimental Section

General Method. Most ^1H NMR spectra were recorded on a Varian T-60 spectrometer, using either CCl_4 or $CDCl_3$ as solvent; chemical shifts are reported in ppm relative to Me_4Si (TMS); ^{119}Sn-NMR were obtained with a Bruker AM 300 instrument at Dortmund University (F.R.G.), in $CDCl_3$ as solvent; chemical shifts are reported in ppm relative to Me_4Sn. Mass spectra were obtained with a Finnigan 3300 f-100 mass spectrometer. Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. Gas chromatographic analyses were performed on a Shimadzu GC-8A or Konik 3000-HRGC instrument with a flame ionization detector and data system Shimatzu CR-6A or Konik 825-318, using a column packed with 5% OV17 on Chromosorb G (1.50 m × 3 mm) or 3% SE30 on Chromosorb P (0.30 m × 3 mm). Irradiation was conducted in a reactor equipped with four 250-W lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Potentiometric titration of halide ions was performed in a pHmeter (Seybold Wien) using an Ag/Ag^+ electrode. The products were isolated by preparative radial thin-layer chromatography. Melting points were obtained with a Büchi 510 apparatus and are not corrected.

Materials. *p*-Chlorotoluene (Aldrich), *p*-bromotoluene (Matheson Coleman & Bell), *p*-iodotoluene (Eastman), *p*-dichlorobenzene (Carlo Erba), *p*-dibromobenzene (Matheson Coleman & Bell), 1-chloronaphthalene (Merck), 2-chloroquinoline (Fluka), *p*-bromoanisole (Fluka), *p*-iodoanisole (Fluka), triphenylphosphine (Aldrich), 1-bromonaphthalene (MCB-reagents), *p*-dinitrobenzene (Fluka), tetraphenyltin (Aldrich), triphenyltin chloride (Aldrich), trimethyltin chloride (Aldrich), and methyl iodide (Fluka) were commercially available and were used as received. Hexaphenylditin was obtained from triphenyltin hydride, but using triethylamine instead of allylamine as solvent,[15] mp 237 °C (lit.[15] mp 229.5–231 °C). Triphenyltin hydride was obtained by reduction of triphenyltin chloride with $LiAlH_4$.[16] Triphenyltin iodide was obtained by iodination of tetraphenyltin using benzene as solvent,[6] mp 119–120 °C (lit.[4] mp 120–121 °C). The nucleophile Ph_3SnNa (**2**) was prepared in liquid ammonia by reaction of different tin compounds (Ph_4Sn, Ph_3SnCl, Ph_3SnI, and $Ph_3SnSnPh_3$) with sodium metal.[4,6] Then nucleophile **2** was trapped with IMe to give Ph_3SnMe to quantify the yield of nucleophile **2** and in all the cases the yields were 90–100%.[4] The reaction with Ph_4Sn was slower than with the other tin compounds. If large amounts of Na metal were used, the yields would not be quantitative, and some Ph_2SnMe_2 would form by reaction of **2** with Na in excess. As the yields were almost quantitative with any of these substrates, we chose Ph_6Sn_2 for most of the reaction with **2**. Me_3Sn^- (**17**) was prepared from Me_3SnCl by the same method as **2**.[5]

Photostimulated Reaction of 2 with *p*-Chlorotoluene. The following procedure is representative of these reactions. The equipment used has been previously described.[3a] To 250 mL of distilled ammonia were added Ph_6Sn_2 (0.4 mmol) and then Na metal (1.0 mmol, 25% excess) in small pieces, waiting for total decoloration between each addition, and 20 min after the last addition (no more solid Ph_6Sn_2) **2** was ready for use (pale yellow solution). *p*-Chlorotoluene (0.8 mmol) dissolved in 1 mL of anhydrous ethyl ether was added to the solution, and the reaction mixture was irradiated for 60 min. The reaction was quenched with an excess of methyl iodide. The ammonia was allowed to evaporate, and water (50 mL) was added to the residue and it was extracted twice with chloroform (50 mL each). The chloride ions in the aqueous solution were determined potentiometrically. The organic extract was quantified by ^1H NMR after the solvent and the volatile compounds were removed by heating the solution

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(13) (a) With carbanionic nucleophiles, as the pK_a increases so does the reactivity toward haloarenes in the initiation step of the $S_{RN}1$ mechanism (higher the HOMO value).[13b] As the pK_a of Me_3SnH (23.5)[13c] is much higher than that of Ph_3SnH (ca. 16)[13c] the former may have higher HOMO than the latter, and the difference in reactivity with haloarenes in separated experiments may be because Me_3Sn^- ion is more reactive in the initiation step of this mechanism. (b) Borosky, G. A.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 247. (c) Petrov, E. S.; Terekhova, M. I.; Mirskov, R. G.; Voronkov, M. G.; Shatenshtein, A. I. *Dokl. Akad. Nauk. SSSR* **1975**, *221*, 111; *Chem. Abstr.* **1975**, *82*, 155040.

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under reduced pressure. Once a quantitative separation of the organic residue by radial TLC (eluted with hexane) was performed, *p*-tolyltriphenyltin (Ph_3SnTo) was obtained in a 55% isolated yield: mp 124–125 °C (lit.[17] mp 124 °C); ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 7.00–8.02 (m, 19 H); MS (70 eV) *m/e* 365 (58), 288 (13), 274 (18), 211 (23), 197 (53), 167 (25), 120 (100), 91 (24), 77 (11).

Inhibited Reaction of 2 with *p*-Chlorotoluene. The procedure was as described above, but *p*-DNB (0.11 mol %) was added to the solution of 2 prior to the addition of *p*-chlorotoluene. After 60 min of irradiation the chloride ion liberated was found in less than 5% yield and no substitution product was detected by ^1H NMR.

Reaction of 2 with *p*-Chlorotoluene in the Dark. The described procedure was followed, except that the reaction flask was wrapped with aluminum foil. The results were the same as those found for the inhibited reaction.

Photostimulated Reaction of 2 with *p*-Iodoanisole. A solution prepared from Ph_6Sn_2 (0.35 mmol) and Na metal was irradiated before slow addition of *p*-iodoanisole (0.70 mmol, dissolved in 2 mL of anhydrous diethyl ether) from a dropping funnel fitted to the original equipment. The reaction mixture was irradiated for 60 min, and then it was quenched with an excess of methyl iodide. Ammonia was allowed to evaporate, dried benzene was added to dissolve the organic components of the reaction mixture, and then the organic phase was filtered. After separation of the reaction mixture using radical TLC, the following were obtained: *p*-anisyltriphenyltin (eluted with diethyl ether/hexane (0.5:99.5)) 14% isolated yield [mp 150–152 °C (lit.[18] mp 151–152 °C); ^1H NMR (CCl_4) δ 3.75 (s, 3 H), 6.80–7.80 (m, 19 H); MS (70 eV) *m/e* 458 (5), 381 (100), 351 (15), 304 (10), 289 (11), 274 (18), 227 (20), 197 (43), 184 (16), 120 (24)] and triphenyltin iodide (eluted with ethyl acetate/hexane (10:90)) [mp 117–121 °C (lit.[4] mp 121 °C); MS (70 eV) *m/e* 401 (2), 351 (100), 247 (7), 197 (17)]. When water together with an organic solvent were used to extract the reaction mixture, bis(triphenyltin) oxide and triphenyltin hydroxide were obtained as coproducts. Bis(triphenyltin) oxide: recrystallized from petroleum ether, mp 123–124 °C (lit.[19] mp 124 °C); ^{119}Sn NMR δ −84.7 (lit.[20] ^{119}Sn NMR δ −82.7); IR 775 cm^{-1} (SnO) (lit.[21] IR 777 cm^{-1}); MS (70 eV) *m/e* 718 (<1), 640 (5), 485 (4), 349 (64), 197 (100), 154 (89), 120 (47). Triphenyltin hydroxide: purified by column chromatography, mp 117.5–119.5 °C (lit.[6] mp 119–120 °C); IR 3616 cm^{-1} (OH).

Photostimulated Reaction of 17 with *p*-Chloroanisole. Nucleophile 17 was prepared in liquid ammonia (lemon yellow solution) from Me_3SnCl (3.5 mmol) and Na metal (8.4 mmol, 20% excess). *p*-Chloroanisole (3.2 mmol, dissolved in 1 mL of anhydrous diethyl ether) was added, and the procedure was as usual but diethyl ether was used as solvent to dissolve the products. After a radial TLC separation, *p*-anisyltrimethyltin was obtained (eluted with petroleum ether, 30–60 °C and evaporated the solvent until constant weight) in an 87% isolated yield: colorless liquid;[22] ^1H NMR ($CDCl_3$, 80.13 MHz) δ 0.26 (s, 9 H, ^2J(SnCH) = 53.7 Hz), 3.80 (s, 3 H), 6.92 and 7.41 (AA′BB′ system, 4 H).

Other substitution tin products isolated from these reactions were the following: *p*-bis(triphenylstannyl)benzene [recrystallized twice from benzene, mp 305.5–307 °C (lit.[23] mp 289–292 °C); MS (30 eV) *m/e* 696 (79), 426 (100), 350 (82), 273 (10), 196 (23) 120 (17)], 1-naphthyltriphenyltin [recrystallized from petroleum ether (30–60 °C), mp 102–105 °C (lit.[17] mp 125 °C); MS (25 eV) *m/e* 400 (100), 352 (28), 324 (10), 247 (20), 204 (22), 197 (52), 120 (80)], 2-quinolyltriphenyltin [recrystallized from petroleum ether (64–66 °C) until constant melting point, mp 115.5–117.0 °C; MS (70 eV) *m/e* 478 (56), 402 (23), 351 (18), 324 (37), 248 (10), 197 (100), 128 (30), 120 (53), 77 (23). Anal. Calcd for $C_{27}H_{21}NSn$: C, 67.82; H, 4.43; N, 2.93. Found: C, 67.8; H, 4.5; N, 2.9. It decomposes partially in contact with silica gel]; *p*-bis(trimethylstannyl)benzene [obtained by radial TLC (eluted with petroleum ether, 40–60 °C), mp 119–121 °C (lit.[5] mp 123–124 °C); ^1H NMR (200 MHz) ($CDCl_3$) δ 0.257 (s, 18 H, $^2J(^{117,119}SnCH)$ 52.78; 55.28 Hz), 7.454 (s, 4 H); ^{13}C NMR δ 9.64 ($-CH_3$), 135.58 (C-2), similar to that reported];[24] 1-naphthyltrimethyltin [vacuum distilled using a Kugelrohr apparatus, colorless liquid[22] ^1H NMR ($CDCl_3$, 90 MHz) δ 0.43 [s, 9 H, $^2J(^{117,119}SnCH)$ = 52.5, 55.5 Hz]], and 2-quinolyltrimethyltin [vacuum distilled using a Kugelrohr apparatus, colorless liquid; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.58 (s, 9 H, ^2J-(^{117,119}SnCH) = 55 Hz), 7.58–8.42 (m, 6 H), similar to that reported;[25] it decomposes fast in contact with silica gel].

Competition Experiments. Relative Reactivity of 2 vs 17. Both nucleophiles were prepared together in liquid ammonia as usual from Me_3SnCl (2.0 mmol), Ph_3SnCl (2.0 mmol), and Na metal (9.9 mol, 24% excess). *p*-Chloroanisole (1.0 mmol) was added dissolved in 1 mL of anhydrous diethyl ether, and after 60 min of irradiation the reaction was quenched with MeI. The reaction mixture was extracted with chloroform and water. Substitution products were quantified as follows: *p*-anisyltrimethyltin (49% yield) by GLC (using *p*-dibromobenzene as internal standard) and *p*-anisyltriphenyltin by separation of the reaction mixture by radial TLC (43% isolated yield).

Relative Reactivity of 17 vs Diphenylphosphide Ions. Diphenylphosphide anion was formed in a first step and trimethyltin anion in a second one. Diphenylphosphide was generated by reaction of triphenylphosphine (2.0 mmol) and sodium in excess,[26] and then Me_3SnCl was added, followed by a new addition of Na metal (4.1 mmol). Before the substrate (*p*-chloroanisole, 1.0 mmol) was added, *tert*-butyl alcohol (ca. 2 mmol) was added to eliminate all the amide anion formed in previous steps. After 60 min of irradiation the reaction was quenched with MeI and extracted with methylene chloride and water. *p*-Anisyltrimethyltin was quantified by GLC (48% yield), and *p*-anisyldiphenylphosphine was quantified as *p*-anisyldiphenylphosphine oxide (44% isolated yield) after oxidation with hydrogen peroxide[26] and separation by radial TLC.

Acknowledgment. C.C.Y. gratefully acknowledges receipt of a fellowship from the Consejo de Investigaciones Cientificas y Técnicas (CONICET). This work was partly supported by the Consejo de Investigaciones de la Provincia de Córdoba, CONICET and Antorchas Foundation.

Registry No. **1a**, 639-58-7; **1b**, 1064-10-4; **2**, 42451-63-8; **3a**, 106-43-4; **3b**, 106-38-7; **3c**, 624-31-7; **3d**, 90-13-1; **3e**, 90-11-9; **3f**, 612-62-4; **4a**, 15807-28-0; **4b**, 81134-67-0; **4c**, 143370-70-1; **7**, 106-46-7; **11**, 96872-40-1; **12**, 106-37-6; **16a**, 623-12-1; **17**, 57064-01-4; **18a**, 940-00-1; **18b**, 944-85-4; **18c**, 79476-04-3; **15**, 595-90-4; **14**, 108-86-1; **19**, 1012-73-3; **20**, 57880-01-0; Na, 7440-23-5; *p*-IAn, 696-62-8; *p*-BrAn, 104-92-7; Ph_2P^-, 6396-02-7; naphthalene, 91-20-3; anisole, 100-66-3; *p*-anisyliphenylphosphine oxide, 795-44-8.

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