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Phenols as Starting Materials for the Synthesis of Arylstannanes via $S_{RN}1$[1]

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Phenols are converted into aryl diethyl phosphate esters (ArDEP), which on reaction with sodium trimethylstannide (**1**) or sodium triphenylstannide (**2**) in liquid ammonia afford arylstannanes by the $S_{RN}1$ mechanism. Thus, the photostimulated reaction of phenylDEP (**3**), (4-methoxyphenyl)DEP (**4**), (4-biphenyl)DEP (**5**), (1-naphthyl)DEP (**6**), (2-naphthyl)DEP (**7**), and 2- (**34**), 3- (**32**), and (4-pyridyl)DEP (**35**) with **1** leads to monostannylated product in fair to excellent yields (20−98%). Also, substrates containing two or three leaving groups react with **1** under irradiation, affording the corresponding di- or tristannylated aryl compounds. With tetraethyl *m*-phenylene bisphosphate (**15**), tetraethyl *p*-phenylene bisphosphate (**21**), (4-chlorophenyl)DEP (**22**), and 1,3,5-tris(diethylphospho)benzene (**30**), the di- or trisubstitution products 1,3-bis(trimethylstannyl)benzene (**19**) (79%), 1,4-bis(trimethylstannyl)benzene (**23**) (95 and 97%), and 1,3,5-tris(trimethylstannyl)benzene (**31**) (57%) are obtained, respectively. Also, the reaction of **6** and **7** with **2** leads to substitution products in quantitative yields, and the reaction of **21**, **22**, and (4-bromophenyl)DEP (**24**) with **2** affords 1,4-bis(triphenylstannyl)benzene (**38**) in high yields (70−100%). On the other hand, the results obtained in the photostimulated reaction of **24** and (4-iodophenyl)DEP (**25**) with **1**, as well as in the reaction of **25** with **2**, clearly indicate a fast HME reaction.

Introduction

The preparation of organotin compounds and its application as intermediates has become a very important aspect in organic chemistry.[2] For example, palladium-catalyzed reactions involving aryltin compounds have found wide application in the synthesis of aromatic and heterocyclic compounds.[3] In connection with the synthetic importance of these reactions, we are interested in searching new routes to arylstannanes.

Aromatic nucleophilic substitution via the $S_{RN}1$ mechanism enables the substitution of appropriate nucleofuges on unactivated aromatic systems with suitable nucleophiles.[4] The proposed mechanism is a chain process (Scheme 1). In the initiation step there is an electron transfer (ET) from the nucleophile to the starting substrate (eq 1). If this ET is not spontaneous, it could be induced by UV light.[4]

The key species of the process, Ar$^{\bullet}$, obtained by the reductive cleavage of $ArX^{\bullet-}$ (eq 2), combines with the nucleophile to give $ArNu^{\bullet-}$ (eq 3), which in turn reduces the starting aromatic substrate. The radical anion $ArX^{\bullet-}$ is regenerated according to reaction 4. It should be noted that the coupling with the nucleophile is not the only reaction that aryl radicals can undergo: hydrogen atom transfer from the solvent is one of the most important side reactions (eq 5). This competitive reaction is prevented by using liquid ammonia as solvent, which is a poor hydrogen atom donor.[4]

Scheme 1

$$ArX + Nu^{-} \longrightarrow (ArX)^{-\bullet} + Nu^{\bullet} \quad (1)$$

$$(ArX)^{-\bullet} \longrightarrow Ar^{\bullet} + X^{-} \quad (2)$$

$$Ar^{\bullet} + Nu^{-} \longrightarrow (ArNu)^{-\bullet} \quad (3)$$

$$(ArNu)^{-\bullet} + ArX \longrightarrow ArNu + (ArX)^{-\bullet} \quad (4)$$

$$Ar^{\bullet} + SH \longrightarrow ArH + S^{\bullet} \quad (5)$$

Triorganostannyl anions have proved to be excellent nucleophiles in $S_{RN}1$ reactions.[5] Application of these reactions to the synthesis of arylstannanes is currently in progress in our laboratory. We have recently described the photostimulated reactions of a number of haloarenes and haloheteroarenes with triphenylstannyl anions in dimethyl sulfoxide (DMSO) and acetonitrile (ACN) as solvents.[6] The photostimulated reactions of 1-chloronaphthalene, 2- and 3-chloropyridines, and 1,4-

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[1] A portion of this work has previously appeared; see: Chopa, A. B.; Lockhart, M. T.; Silbestri G. *Organometallics* **2000**, *19*, 2249.

[2] (a) Davies, A. G. *Organotin Chemistry*; VCH: Weinheim, 1997. (b) Sato, S. *Comprehensive Organometallic Chemistry II*; Pergamon: New York, 1995; Vol. 8.

[3] For a review see: Farina V.; Krishnamurthy V.; Scott W. J. The Stille Reaction. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1997; Vol. 50.

[4] For reviews see: (a) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283. (b) Norris, R. K. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 4, p 451. (c) Rossi, R. A.; Pierini, A. B.; Santiago, A.N. Aromatic Substitution by the $S_{RN}1$ Reaction. In *Organic Reactions*; Paquette, L. A., Bittman, R., Eds.; John Wiley & Sons: New York, 1999; Vol. 54, p 1.

[5] Córsico, E. F.; Al Postigo; Rossi, R. A. *Molecules* **2000**, *5*, 1076

[6] Lockhart, M. T.; Chopa, A. B.; Rossi, R. A. *J. Organomet. Chem.* **1999**, *582*, 229

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dichlorobenzene with potassium triphenylstannide (Ph_3SnK) lead to high yields (70−90%) of the corresponding mono- or distannylated benzenes. The reactions of arylbromides (ArBr) and aryliodides (ArI) in the dark or under irradiation lead only to dehalogenation products through a halogen metal exchange (HME) mechanism. In general the reactions in DMSO give better yields than in ACN, probably because the hydrogen abstraction reaction by aryl radicals from ACN competes with the coupling reaction with Ph_3Sn^- ions.

We have also studied the reactions of several aryltrimethylammonium salts with trimethylstannyl anions in liquid ammonia.[7] Arylamines are converted into aryltrimethylammonium salts, which on reaction with sodium trimethylstannide (Me_3SnNa) in liquid ammonia afford aryltrimethylstannanes by the $S_{RN}1$ mechanism in good to excellent yields (45−100%).

In the course of our investigations we have found that the photochemically induced reaction of some aryl diethyl phosphate esters (ArDEP) with trimethyl- and triphenylstannyl anions in liquid ammonia[1] proceeds cleanly via an $S_{RN}1$ mechanism. All these substrates, under the reaction conditions studied, gave substitution products in excellent yields (70−100%). The main advantage of these reactions is that they enable the direct synthesis of organostannanes with different aryl ligands,[4] avoiding the use of organomagnesium or organolithium reagents. It is known, for example, that the reaction of 2-halopyridines with *n*-butyllithium followed by the reaction with a triorganostannyl chloride led to the corresponding organostannane in low yield due to the formation of complex mixtures of intermediates during the lithiation process.[8]

Further studies on the reaction of aryl diethyl phosphate esters with triphenyl- and trimethylstannylsodium have revealed that this would be a convenient method for the synthesis of mono-, di-, and tristannylated aryl- and heteroaryl compounds.

In this paper, we report the results obtained and the mechanistic aspects of the reactions of several mono-, di-, and trisubstituted ArDEP with trimethyl- (**1**) and triphenylstannyl (**2**) anions in liquid ammonia.

Results and Discussion

Aryl and heteroaryl diethyl phosphate esters were prepared in high yields from the corresponding phenols.[9] Triorganostannyl anions were generated from the appropriate triorganostannyl chloride according to the reaction conditions established in previous work.[7] Reactions were conducted without irradiation (dark) and under irradiation. The experiments were run under nitrogen or argon, and the product compositions were monitored by gas chromatography.

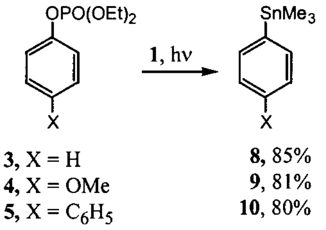
Reactions with Trimethyltin Sodium (1). The results obtained are summarized in Table 1. Photostimulated reaction of phenylDEP (**3**) with **1** proceeded smoothly (2 h) to afford phenyltrimethylstannane (**8**) in 85% yield (entry 1).

Table 1. Reaction of Aryl- and Heteroaryl Diethyl Phosphates with Me_3SnNa in Liquid Ammonia[a]

entry	aryl moiety	conditions time (h)	$Ar-SnMe_3$, yield %[b]
1	C_6H_5	*hν*, 2	C_6H_5-$SnMe_3$, 85
2	4-$MeOC_6H_4$	*hν*, 1	4-MeO-C_6H_4-$SnMe_3$, 81
3	4-biphenyl	*hν*, 1	4-biphenyl-$SnMe_3$, 80
4	1-$C_{10}H_7$	*hν*, 1	1-$C_{10}H_7$-$SnMe_3$, 93
5	2-$C_{10}H_7$	*hν*, 1	2-$C_{10}H_7$-$SnMe_3$, 98
6	4-$MeCOC_6H_4$	*hν*, 2	0[c]
7	4$MeOOCC_6H_4$	*hν*, 2	0[c]
8	1,3-C_6H_4[d]	*hν*, 4	1,3-$(Me_3Sn)_2$-C_6H_4, 79[e]
9	1,4-C_6H_4[d]	*hν*, 1	1,4-$(Me_3Sn)_2$-C_6H_4, 95[e]
10	4-ClC_6H_4[d]	*hν*, 1	1,4-$(Me_3Sn)_2$-C_6H_4, 97[e]
11	4-BrC_6H_4[d]	*hν*, 1.5	C_6H_5-$SnMe_3$, 37[g]
12	4-BrC_6H_4[d]	dark, 1.5	0[h]
13	4-IC_6H_4[d]	*hν*, 1.5	C_6H_5-$SnMe_3$, 26[g]
14	4-IC_6H_4[d]	dark, 1.5	0[i]
15	1,3,5-C_6H_3[f]	*hν*, 6	1,3,5-$(Me_3Sn)_3C_6H_3$, 57[j]
16	2-pyridyl	*hν*, 4	2-Me_3Sn pyridine, 35
17	3-pyridyl	*hν*, 3	3-Me_3Sn pyridine, 74
18	4-pyridyl	*hν*, 5	4-Me_3Sn pyridine, 20

[a] Substrate/Me_3SnNa, 1:1.2. There is no reaction in the dark, except were it is stated. [b] Determined by GC. [c] Complex mixtures. [d] Substrate/Me_3SnNa, 1:2.2. [e] Isolated yield. [f] Substrate/Me_3SnNa, 1:3.3. [g] Together with **3** and **29**. [h] **3**, 79%. [i] **3**, 83%. [j] Together with traces of disubstitution product.

Similar results were obtained in the reactions of (4-methoxyphenyl)DEP (**4**), (4-biphenyl)DEP (**5**), (1-naphthyl)DEP (**6**), and (2-naphthyl)DEP (**7**) with **1**. Thus, under irradiation, the corresponding substitution products (4-methoxyphenyl)trimethylstannane (**9**), (4-biphenyl)trimethylstannane (**10**), (1-naphthyl)trimethylstannane (**11**), and (2-naphthyl)trimethylstannane (**12**) were formed in excellent yields (entries 2−5), according to eqs 6 and 7. The NMR spectra of the reaction mixtures showed no signals corresponding to the other possible isomers, indicating the complete regioselectivity of the substitution. When these reactions were carried out in the dark, the corresponding starting materials were almost completly recovered. These results suggest that these reactions occur through an $S_{RN}1$ mechanism.



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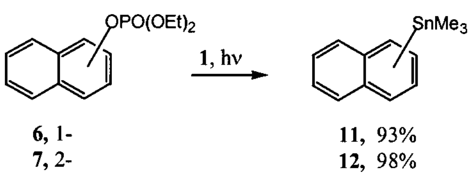

(7)

On the other hand, the photostimulated reaction of (4-acetylphenyl)DEP (**13**) with **1** gave (2 h) a complex reaction mixture, from which could not be detected neither the expected stannylated derivative nor the starting material. Similar results were obtained in the reaction of (4-carbomethoxyphenyl)DEP (**14**) with **1** (entries 6 and 7).

We have also found that there is no reaction between tetraethyl *m*-phenylene bisphosphate (**15**) and **1** in the

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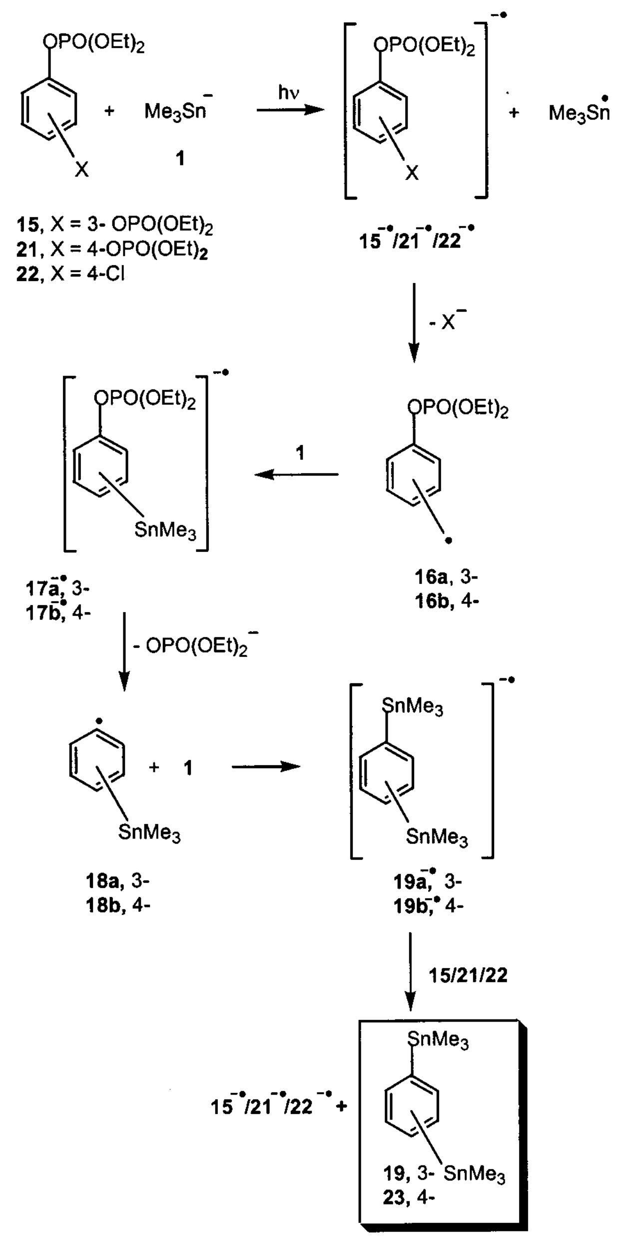
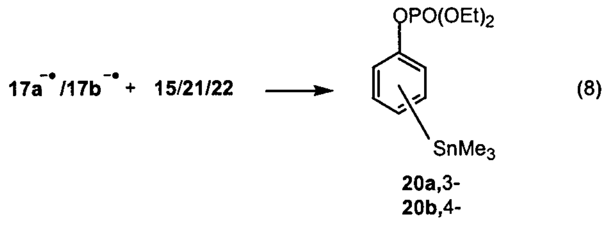
(7) Chopa, A. B.; Lockhart, M. T.; Silbestri, G. *Organometallics* **2001**, *20*, 3358.

(8) (a) Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988. (b) Hughes, D. L.; Verhoeven, T. R. *Tetrahedron Lett.* **1996**, *37*, 2537.

(9) Kenner, G. W.; Williams, N. R. *J. Chem. Soc.* **1955**, 522.

Scheme 2



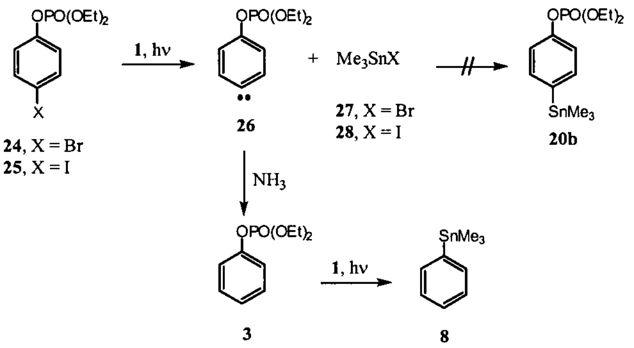


(8)

dark (4 h). However, under irradiation in the same time period, the disubstitution product 1,3-bis(trimethylstannyl)benzene (**19**) was obtained in 79% yield (entry 8). These results clearly indicate that this disubstituted substrate also reacts with **1** by the $S_{RN}1$ mechanism, as shown in Scheme 2.

It should be noted that no monosubstitution product was detected. The absence of monosubstituted product **20a** could be attributed to preferential expulsion of the nucleofuge from the intermediate radical anion **17a** to form radical **18a** rather than ET to **15** (eq 8).

Scheme 3

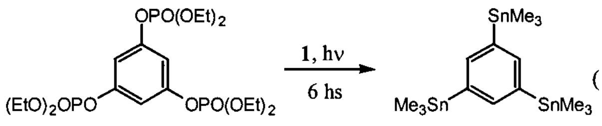


$$\mathbf{27/28} + \mathbf{1} \longrightarrow \underset{\mathbf{29}}{Me_3SnSnMe_3} \qquad (9)$$

As reported in our preliminary communication, similar results have been obtained in the reactions carried out with tetraethyl *p*-phenylenebisphosphate (**21**) and (4-chlorophenyl)DEP (**22**) (entries 9 and 10).

In contrast, (4-bromophenyl)DEP (**24**) and (4-iodophenyl)DEP (**25**) react with **1**, under irradiation, to give a mixture of **3** (38% and 53%, respectively) and **8** (37% and 26%, respectively). Neither monosubstitution (**20b**) nor disubstitution (**23**) products were detected (entries 11 and 13). The reactions of **24** and **25** with **1** in the dark lead only to dehalogenation product **3** (entries 12 and 14). Under both reaction conditions hexamethyldistannane (**29**) was also identified as a significant reaction product. These results suggest a fast HME reaction followed by the protonation of the intermediate anion **26** by the ammonia to give **3**. Under irradiation **3** reacts with **1**, leading to **8** through an $S_{RN}1$ mechanism. The fact that no monosubstitution product **20b** is found indicates that **26** does not react with Me_3SnBr (**27**) or Me_3SnI (**28**) in liquid ammonia (Scheme 3). The formation of **29** is probably due to the reaction between **27** or **28** with **1** (eq 9).

We have also found that a substrate containing three leaving groups reacts with **1** under irradiation to afford the corresponding trisubstituted product. Thus, 1,3,5-tris(diethylphospho)benzene (**30**) led after 6 h to 1,3,5-tris(trimethylstannyl)benzene (**31**, 57%) (eq 10). It is to be noted that traces of disubstitution product were detected (ca. 1% by GC) and that no reaction occurred in the dark (entry 15). Recently, Rossi has reported the synthesis of **31** by the reaction of 1,3,5-trichlorobenzene with an excess of **1** in liquid ammonia, under irradiation.[10]



(10)

30 **31**, 57%

We have studied the reaction of some pyridyl derivatives with **1**, to investigate the possible utility of these reactions in the synthesis of (trimethylstannyl)pyridines. It can be observed in Table 1 that the best results were obtained in the photostimulated reaction of (3-pyridyl)DEP (**32**) with **1**, which led to (3-pyridyl)tri-

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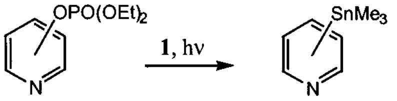
(10) Córsico, E. F.; Rossi, R. A. *Synlett* **2000**, 227–229.

Table 2. Reaction of Aryldiethyl Phosphates with Ph_3SnNa in Liquid Ammonia[a]

entry	aryl moiety	conditions, time (h)	Ar−$SnPh_3$, yield %
1	1-$C_{10}H_7$	*hν*, 4	1-Ph_3Sn-$C_{10}H_7$, 100[b]
2	2-$C_{10}H_7$	*hν*, 6	2-Ph_3Sn-$C_{10}H_7$, 100[b]
3	1,4-C_6H_4[c]	*hν*, 2	1,4-$(Ph_3Sn)_2C_6H_4$, 70[d]
4	4-ClC_6H_4[c]	*hν*, 1.5	1,4-$(Ph_3Sn)_2C_6H_4$, 100[d]
5	4-BrC_6H_4[c]	*hν*, 1.5	1,4-$(Ph_3Sn)_2C_6H_4$, 100[d]
6	4-IC_6H_4[c]	dark, 0.5	0[e]
7	4-IC_6H_4[c]	*hν*, 0.5	C_6H_5-$SnPh_3$, 40[b,f]

[a] Substrate/Ph_3SnNa, 1:1.2; no substitution products were detected without irradiation. [b] Determined by GC. [c] Substrate/Ph_3SnNa, 1:2.2. [d] Isolated yield. [e] A mixture of **3** and $(Ph_3Sn)_2O$. [f] Together with **3**, 52%.

methylstannane (**35**) in 74% yield after 3 h. The photostimulated reaction of (2-pyridyl)DEP (**33**) and (4-pyridyl)DEP (**34**) with **1** led to (2-pyridyl)trimethylstannane (**36**) (4 h) and (4-pyridyl)trimethylstannane (**37**) (5 h) in lower yields (entries 16−18) (eq 11). When these reactions were carried out in the dark, no substitution product was detected. From the above mentioned results it is evident that these reactions take place through an $S_{RN}1$ mechanism.

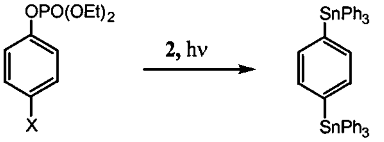


(11)

32, 3- **35,** 74%
33, 2- **36**, 35%
34, 4- **37**, 20%

Reactions with Triphenyltin Sodium (2). In Table 2 it can be seen that the photostimulated reactions of **6**, **7**, **21**, **22**, and **24** with **2** gave the expected stannylated derivatives in excellent yields. When these reactions were carried out in the dark, no substitution product was detected.

The reactions of compounds **21**, **22**, and **24**, i.e., substrates containing two leaving groups, led to the disubstitution product 1,4-bis(triphenylstannyl)benzene (**38**), in 70−100% yield, according to eq 12. No monosubstitution product has been formed. All of these observations strongly suggest that these reactions also take place through an $S_{RN}1$ mechanism.



(12)

21, X = OPO(OEt)$_2$ **38**
22, X = Cl
24, X = Br 70 - 100 %

On the other hand, the reaction of **25** with **2** in the dark led to a mixture of phenylDEP (**3**) with triphenyltin hydroxide and bis(triphenyltin)oxide (entry 6). It should be noted that without adding water during the workup it was possible to isolate triphenyltin iodide as product. These results clearly suggest a fast HME reaction in the dark. To know if the ET process could compete with the HME mechanism, we added **25** to a solution of **2** under irradiation.[11] Reaction products were tetraphenylstannane (**39**, 40%) and **3** (52%) (entry 7). This result indicates that the reaction goes through steps similar to those proposed for the reaction of **25** with **1** (Scheme 3). That is, in a first step the HME reaction operates with **25**, leading to **3**. Under irradiation **3** reacts with **2**, leading to **39** through an $S_{RN}1$ mechanism. The fact that no monosubstitution product, i.e., 4-(triphenylstannyl)phenyl DEP (**40**), is found indicates that the intermediate anion and Ph_3SnI do not react in liquid ammonia.

Conclusions

The present results demonstrate that the diethyl phosphate group can act as a nucleofuge in the reaction of arylDEP esters with trimethyl- and triphenyltin anions in liquid ammonia under irradiation and that these reactions take place through an $S_{RN}1$ mechanism. The attractive feature is that a triorganostannyl group (Me_3Sn− and Ph_3Sn−) can, with interposition of one additional step, be introduced in place of a phenolic hydroxy group. In the first step phenols are converted to the corresponding arylDEP esters with high yields (85−90%). In the second step, in most of the cases we have examined, the substitution reactions led to the corresponding mono-, di-, or tristannylated substrates in 50−100% yield. The synthesis of arylstannanes following this method has the advantage that both operational steps can be performed at moderate temperature, so it should be feasible for use with thermally labile molecules.[12]

The experiments carried out indicate, qualitatively, that **1** is more reactive than **2** in $S_{RN}1$ reactions. For example, compare experiments 4, 5, 9, and 10 in Table 1 with experiments 1−4 in Table 2. These results are in agreement with those obtained by Rossi in the reaction between haloarenes and organotin anions.[13]

Experimental Section

General Procedures. Irradiation was conducted in a reactor made of Pyrex, equipped with four 250 W UV lamps emitting maximally at 350 nm, water-cooled. Proton NMR spectra were recorded on a Bruker AC 200 spectrometer, using $CDCl_3$ as solvent. Mass spectra were obtained with a GC/MS HP 6890. Infrared spectra were recorded on a Nicolet-Nexus FTIR. Most of the reagents were commercially available. Aryl diethyl phosphate esters were prepared by the method of Kenner[9] and characterized by IR and proton NMR spectroscopy.[14] All the products obtained were characterized by comparison of their MS and proton NMR spectroscopic characteristics with those of an authentic sample prepared by known procedures, i.e., **8**,[7] **9**,[13] **10**,[15] **11**,[7] **12**,[16] **19**,[10] **31**,[10] **35**,[17]

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(11) The best conditions for the $S_{RN}1$ mechanism.

(12) Further work is in progress.

(13) Yammal, C. C.; Podestá, J. C.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 5720.

(14) The IR spectra of the esters (as films) present characteristic absorption at 1030, 1155−1164, 1183−1214, and 1265−1274 cm^{-1}. The ^1H NMR spectra present a double triplet at 1.35−1.51 ppm ($^3J_{H,H}$ = 7.0−7.2 Hz, $^4J_{H,P}$ = 1.1 Hz) and a double quartet at 4.25−4.45 ppm ($^3J_{H,H}$ = 7.0−7.2 Hz, $^3J_{H,P}$ = 8.1−8.4 Hz) as well as the absorption due to the aryl groups.

(15) Seyferth, D.; Sarafidis, C.; Evnin, A. B. *J. Organomet. Chem.* **1964**, *2*, 417.

(16) Buchman, O.; Grosjean, M.; Nasielski, J. *Bull. Soc. Chim. Belges* **1962**, *71*, 467.

(17) Yamamoto, Y.; Yanagi, A. *Chem. Pharm. Bull.* **1982**, *30*, 1731.

36,[7] **37**,[17] and **38**.[6] In most cases the yields were determined by GC using the external standard method, but in a few they were by isolation and weighing. To carry out the reactions in the dark, the reaction flask was wrapped with aluminum foil.

Photostimulated Reaction of (4-Biphenyl) Diethyl Phosphate (5) with Me_3SnNa (1). The reactions were performed following the same procedure in all cases.

Sodium-dried ammonia (150 mL) was condensed into a 250 mL two-necked, round-bottomed Pyrex flask equipped with a coldfinger condenser, a nitrogen inlet, and a magnetic stirrer. Me_3SnCl (0.219 g, 1.1 mmol) was dissolved in the ammonia, and Na metal (0.058 g, 2.53 mg atom) was added until a blue color persisted for at least 5 min. When the blue color disappeared, **5** (0.293 g, 1.00 mmol) was added and then the mixture irradiated with stirring, for 5 h. The reaction was quenched by adding MeI in excess, and ammonia was allowed to evaporate. The residue was treated with water and then extracted with ether. Ether extracts were washed with an aqueous saturated solution of NaCl and dried over $MgSO_4$. The ether was removed and the residue was recristallized in ethanol, yielding 0.250 g (0.79 mmol, 79%) of (4-biphenyl)-trimethylstannane (**10**), mp 47−49 °C (lit.[15] mp 46−47 °C).

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Supporting Information Available: NMR and MS data of trimethylstannyl derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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