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Two-Step Synthesis of Arylstannanes from Phenols

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Summary: Phenols are converted into aryl diethyl phosphates, which on reaction with alkali-metal triorganostannides in liquid ammonia afford arylstannanes in excellent yield.

$S_{RN}1$ (Unimolecular Radical Nucleophilic Substitution) is a well-known process.[1] The proposed mechanism is a chain process (Scheme 1). Triorganostannyl anions have proved to be excellent nucleophiles in $S_{RN}1$ reactions.[2] We have recently described the photostimulated reactions of haloarenes and haloheteroarenes with triphenylstannyl anions in dimethyl sulfoxide, which gave substitution products in good to excellent yield.[3] The main advantage of these reactions is that they enable the direct synthesis of organostannanes with different aryl ligands,[1] avoiding the use of organomagnesium or organolithium reagents.

Scheme 1

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

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

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

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

Although halogens are by far the most commonly used leaving groups in $S_{RN}1$ reactions, other leaving groups, including $(EtO)_2P(O)O$,[1] have been used.

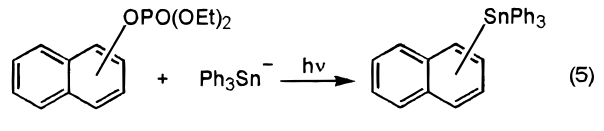
We report here the results obtained in reactions of a number of aryl diethyl phosphates (ArDEP)[5] with (triphenylstannyl)sodium (**1**) and (trimethylstannyl)sodium (**2**) in liquid ammonia. These reactions are of interest not only from a mechanistic point of view but also as a suitable synthetic route to arylstannanes. As far as we know, there are no reports in the literature concerning the reaction between triorganotin anions and aryldiethyl phosphate esters. The increasing importance of arylstannanes in recent years is connected with their use as substrates in palladium-catalyzed reactions.[6]

Table 1. Reaction of Aryl Diethyl Phosphates with Ph_3SnNa in Liquid Ammonia[a]

entry	aryl moiety	conditions, time (h)	$ArSnPh_3$, yield (%)
1	1-$C_{10}H_8$	*hν*, 4	1-Ph_3Sn-$C_{10}H_8$, 66[b]
2	1-$C_{10}H_8$	*hν*, 4[c]	1-Ph_3Sn-$C_{10}H_8$, 100[b]
3	1-$C_{10}H_8$	dark, 4	0
4	2-$C_{10}H_8$	*hν*, 6	2-Ph_3Sn-$C_{10}H_8$, 73[b]
5	2-$C_{10}H_8$	*hν*, 6[c]	2-Ph_3Sn-$C_{10}H_8$, 100[b]
6	2-$C_{10}H_8$	dark, 6	0
7	1,4-C_6H_4[d]	*hν*, 5	1,4-$(Ph_3Sn)_2$-C_6H_4, 45[e]
8	1,4-C_6H_4[d]	*hν*, 2[c]	1,4-$(Ph_3Sn)_2$-C_6H_4, 70[e]
9	1,4-C_6H_4[d]	dark, 2	0
10	4-BrC_6H_4[d]	*hν*, 1.5	1,4-$(Ph_3Sn)_2$-C_6H_4,100[e]
11	4-BrC_6H_4[d]	dark, 1.5	0

[a] Substrate/Ph_3SnNa = 1/1.2. [b] Determined by GC. [c] Na metal added. [d] Substrate/Ph_3SnNa = 1/2.2. [e] Isolated yield.

We have found that under irradiation (1-naphthyl)-DEP (**3**) reacts with **1** to give the corresponding substitution product, (1-naphthyl)triphenylstannane (**5**) (4 h, 66%).[7] There is no reaction in the dark. It was observed that the addition of ca. 0.01 g (0.43 mmol) of sodium to the reaction mixture before irradiation increased the yield to 100%.[8] Similar results were obtained using (2-naphthyl)DEP (**4**), which after 6 h led to (2-naphthyl)-triphenylstannane (**6**) in quantitative yield (Table 1, entries 1−6) according to eq 5. These results suggest that these reactions take place by the $S_{RN}1$ mechanism.



3: 1-OPO(OEt)$_2$
4: 2-OPO(OEt)$_2$
1
5: 1-SnPh$_3$
6: 2-SnPh$_3$

We have also found that substrates containing two leaving groups react with **1** under irradiation to afford

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[1] 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.; Wiley: New York, 1999; Vol. 54, p 1.

[2] Yammal, C. C.; Podestá, J. C.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 5720.

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

[4] (Triphenylstannyl)- and (trimethylstannyl)sodium were generated by the reaction of sodium with the corresponding triorganostannyl chloride (R_3SnCl) in liquid ammonia.[2]

[5] Phenols were converted into the corresponding aryl diethyl phosphate esters by the reaction with diethyl phosphite and triethylamine in CCl_4 solution. See: Kenner, G. W.; Williams, N. R. *J. Chem. Soc.* **1955**, 522.

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

[7] Irradiation was conducted in a reactor equipped with four 250 W water-cooled UV lamps emitting maximally at 350 nm. The reactions were performed by following the same procedure in all cases: 200 mL of sodium-dried ammonia was condensed into a 500 mL three-necked, round-bottomed Pyrex flask equipped with a coldfinger condenser, a nitrogen inlet, and a magnetic stirrer. Ph_3SnCl (0.92 g, 2.4 mmol) and Na metal (0.126 g, 5.50 mg atom) were added. When the blue color disappeared, **3** (0.560 g, 2.00 mmol) was added and then the mixture irradiated with stirring, for 4 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. The product was quantified by GC using the external standard method, compared with an authentic sample prepared by a known procedure.[3]

10.1021/om000013l CCC: $19.00

Scheme 2

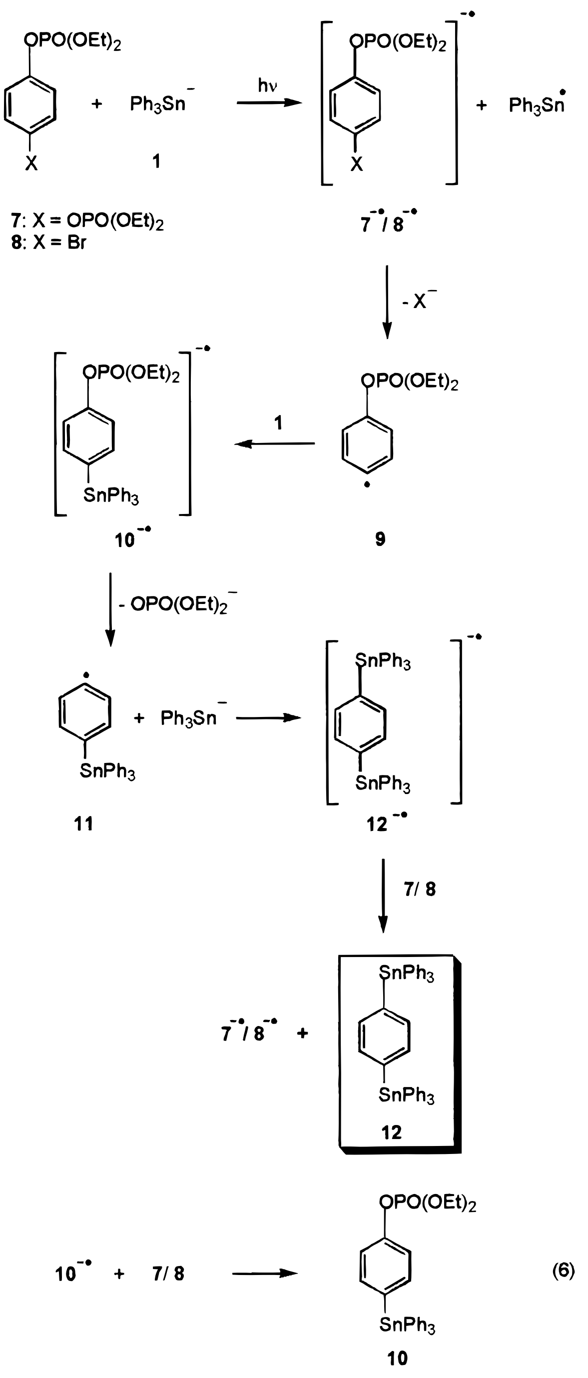

Table 2. Reaction of Aryl Diethyl Phosphates with Me_3SnNa in Liquid Ammonia[a]

entry	aryl moiety	conditions[b]	$ArSnMe_3$, yield (%)
1	$4\text{-}MeOC_6H_4$	*hν*	Me_3Sn(*p*-anisyl), 81[c]
2	$4\text{-}MeOC_6H_4$	dark	0
3	$1\text{-}C_{10}H_8$	*hν*	$1\text{-}Me_3Sn\text{-}C_{10}H_8$, 93[c]
4	$1\text{-}C_{10}H_8$	dark	0
5	$4\text{-}ClC_6H_4$[d]	*hν*	$1,4\text{-}(Me_3Sn)_2\text{-}C_6H_4$, 97[e]
6	$4\text{-}ClC_6H_4$[d]	dark	0
7	$1,4\text{-}C_6H_4$[d]	*hν*	$1,4\text{-}(Me_3Sn)_2\text{-}C_6H_4$, 95[e]
8	$1,4\text{-}C_6H_4$[d]	dark	0

[a] Substrate/Me_3SnNa = 1/1.2. [b] Reaction time: 1 h. [c] Determined by GC. [d] Substrate/Me_3SnNa = 1/2.2. [e] Isolated yield.

disubstitution products in good to excellent yield. Thus, 1,4-bis(diethylphosphono)benzene (**7**) led after 5 h to 1,4-bis(triphenylstannyl)benzene (**12**;[9] 45%). Stimulation by the addition of sodium increased the yield to 70% after a 2 h reaction time. It is to be noted that no monosubstitution product was detected and that no reaction occurred in the dark (Table 1, entries 7−9). Similar results were obtained with (4-bromophenyl)DEP (**8**): there was no reaction with **1** in the dark, but under irradiation the disubstitution product **12** was obtained in quantitative yield (Table 1, entries 10 and 11). All these results clearly indicate that these disubstituted substrates also react with **1** under irradiation by the $S_{RN}1$ mechanism, as shown in Scheme 2.

The fact that in these reactions monosubstitution products were not detected suggests that the fragmentation reaction of $\mathbf{10}^{\bullet-}$ to give **11** is faster than the electron transfer (ET) to **7** or **8** (Scheme 2, eq 6).

The reactions between **2** and various ArDEP esters gave similar results.

In Table 2 it can be observed that (4-methoxyphenyl)-DEP (**13**), **3**, (4-chlorophenyl)DEP (**14**), and **7** did not react with **2** in the dark (1 h) (entries 2, 4, 6, and 8), but under irradiation the corresponding substitution products (4-methoxyphenyl)trimethylstannane (**15**),[10] (1-naphthyl)trimethylstannane (**16**)[11] and 1,4-bis(trimethylstannyl)benzene (**17**)[11] were formed in high yield (81%, 93%, 97%, and 95%, respectively) (entries 1, 3, 5, and 7). No monosubstitution products were detected in the reaction of **14** and **7**. These results suggest that these reactions also occur through an $S_{RN}1$ mechanism.

The obtained results demonstrate that the conversion of phenols into the corresponding aryl diethyl phosphates followed by the $S_{RN}1$ displacement with organotin anions is an excellent and convenient method for the synthesis of arylstannanes. This method has the advantage that both operational steps can be performed at moderate temperature and various substituents in the aromatic ring are tolerated. Further work is in progress to study the scope of the reaction.

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(8) An alkali metal dissolved in liquid ammonia exists for the most part as alkali-metal cations and solvated electrons and is effective in provoking $S_{RN}1$ reactions. See: Dye, J. L. *Acc. Chem. Res.* **1968**, *1*, 306.

(9) Quantified by GC by comparison with an authentic sample.[3]

(10) Quantified by GC by comparison with an authentic sample prepared according to: Eaborn, C.; Hornfeld, H.; Watson, D. R. M. *J. Chem. Soc. B* **1967**, 1036.

(11) NMR spectroscopic data are in agreement with those reported in the literature.[2]