

# Synthesis of Bis(trimethylstannyl)aryl Compounds via an S<sub>RN</sub>1 Mechanism with Intermediacy of Monosubstitution Products

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1,2-Bis(trimethylstannyl)benzene (**1**) and 2,2'-bis(trimethylstannyl)-1,1'-binaphthyl (**2**), useful as intermediates in the preparation of bidentate Lewis acids, have been synthesized from simple phenols through a two-step sequence. Thus, 2-chlorophenol, 1,2-dihydroxybenzene, and binaphthol were converted into the corresponding aryl diethyl phosphate esters **4–6**, which on reaction with sodium trimethylstannide (**3**) in liquid ammonia, under irradiation, afforded **1** and **2**, respectively, in good yields (66–82%). The results obtained clearly indicate that the reactions proceed through an S<sub>RN</sub>1 mechanism and involve the intermediacy of a monosubstitution product.

## Introduction

In recent years the synthesis of multidentate Lewis acids has been a subject of growing interest. Studies carried out by Jurkschat et al.<sup>1</sup> have demonstrated that 1,2-bis(haloorganostannyl)benzenes work as powerful bidentate Lewis acids toward halide ions. On the other hand, preliminary work carried out by Kuivila et al.<sup>2</sup> showed that 2,2'-binaphthyl-substituted organotin Lewis acids are interesting molecules, taking into account that the rotation about the C(1)–C(1') bond should allow the two metal centers to interact with ligands of different size. The haloorganostannyl derivatives studied by both groups were synthesized from the corresponding bis(trimethylstannyl) compounds through methyl/chlorine exchange reactions.

The methods available for the synthesis of such bis(trimethyltin) compounds are relatively limited. Thus, the preparation of 1,2-bis(trimethylstannyl)benzene (**1**) was first described by Seyferth in 1966, via a Diels–Alder reaction between bis(trimethylstannyl)ethyne and  $\alpha$ -pyrone in 51% yield.<sup>3</sup> Kuivila synthesized **1** (42%) by the reaction of 1,2-dibromobenzene with Me<sub>3</sub>SnNa in tetraglyme.<sup>4</sup> This procedure was modified by Jurkschat,<sup>1</sup> who obtained **1** in 67% yield by the reaction (42 h) of 1,2-dichlorobenzene with Me<sub>3</sub>SnNa in THF. Recently, Rossi<sup>5</sup> reported that the photostimulated reaction of 1,2-dichlorobenzene with Me<sub>3</sub>SnNa in liquid ammonia afforded the disubstitution product **1** in 58% yield, together with trimethylphenylstannane (35%).

On the other hand, 2,2'-bis(trimethylstannyl)-1,1'-binaphthyl (**2**) has been prepared by Kuivila<sup>2</sup> by the

reaction of 2,2'-dilithio-1,1'-binaphthyl with excess Me<sub>3</sub>SnCl at –78 °C (87%, 12 h).

We have proved that haloarenes and haloheteroarenes,<sup>6</sup> aryl- and heteroaryl diethyl phosphates,<sup>7,8</sup> and aryl- and heteroaryl trimethylammonium salts<sup>9</sup> could be excellent starting materials for the synthesis of mono-, di-, and tristannylated substrates by an S<sub>RN</sub>1 mechanism. The main advantage of these reactions is that they enable the direct synthesis of organostannanes with different aryl ligands, avoiding the use of organo-magnesium or organolithium reagents.

The fact that aryl diethyl phosphate esters containing two nucleofuges have been shown to react quite efficiently with trimethyltin sodium (Me<sub>3</sub>SnNa; **3**) by the S<sub>RN</sub>1 mechanism, leading to the corresponding distannylated products,<sup>8</sup> prompted us to study the scope of this reaction in the synthesis of compounds **1** and **2**. The present work describes the synthesis of **1** and **2** by a photochemically induced reaction between aryl diethyl phosphate esters and **3** in liquid ammonia and some important mechanistic aspects of these reactions.

## Results and Discussion

We studied the reaction of 2-(chlorophenyl) diethyl phosphate (**4**), 1,2-phenylene bis-(diethyl phosphate) (**5**) and 2,2'-bis(diethylphosphoxy)-1,1'-binaphthyl (**6**) with **3** in liquid ammonia.

The results obtained using compounds **4** and **5** are summarized in Table 1. The photostimulated reaction of **4** with **3** (1/2.2 ratio) proceeded smoothly (1.5 h) to afford 1,2-bis(trimethylstannyl)benzene (**1**)<sup>10</sup> in 63% yield (entry 1). When this reaction was carried out in

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(1) Altmann, R.; Jurkschat, K.; Schürman, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 5858 and references therein.

(2) Krishnamurti, R.; Kuivila, H. G.; Shaik, N. S.; Zubieta, J. *Organometallics* **1991**, *10*, 423.

(3) Evin, A. B.; Seyferth, D. *J. Am. Chem. Soc.* **1966**, *89*, 952.

(4) Wursthorn, K. R.; Kuivila, H. G. *J. Organomet. Chem.* **1977**, *140*, 29.

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

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(8) Chopa, A. B.; Lockhart, M. T.; Dorn, V. B. *Organometallics* **2002**, *21*, 1425.

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

(10) NMR spectroscopic data are in agreement with those reported in the literature.<sup>1</sup>

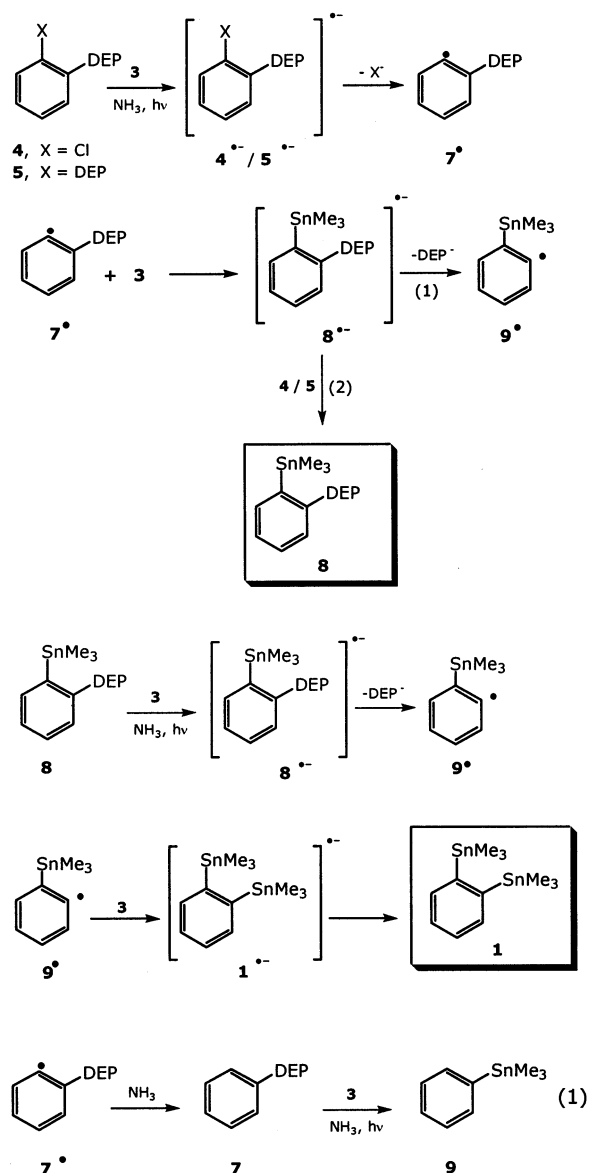
**Table 1. Reactions of 1,2-Disubstituted Aryl Diethyl Phosphates (ArDEP) with Me<sub>3</sub>SnNa in Liquid Ammonia<sup>a</sup>**

entry	substrate (amt, mM)	conditions (time, min)	2-(Me <sub>3</sub> Sn)phenyl-DEP (%) <sup>b</sup>	1,2-(Me <sub>3</sub> Sn)-C <sub>6</sub> H <sub>5</sub> (%) <sup>b</sup>
1	4 (5.88)	hν (90)	0	63 <sup>c</sup>
2	4 (5.88)	dark (90)	12	d <sup>f</sup>
3	4 (5.88)	dark (90) <sup>e</sup>	0	0
4	4 (5.88)	hν (15)	39	11 <sup>f</sup>
5	4 (5.88)	hν (5)	15	d <sup>f</sup>
6	4 (11.89) <sup>g</sup>	hν (90)	36	<3
7	4 (5.88) <sup>g</sup>	hν (90)	45	6
8	4 (1.78) <sup>g</sup>	hν (90)	0	50
9	4 (5.88) <sup>h</sup>	hν (90)	0	66 <sup>c</sup>
10	4 (1.78)	hν (90)	0	50 <sup>i</sup>
11	5 (5.88)	dark (210)	0	0
12	5 (5.88)	hν (210)	0	67 <sup>c</sup>
13	5 (5.88)	hν (90)	36	21 <sup>f</sup>
14	5 (5.88) <sup>h</sup>	hν (210)	0	65

<sup>a</sup> Substrate/Me<sub>3</sub>SnNa = 1/2.2, except where stated. <sup>b</sup> Determined by GC. <sup>c</sup> Together with traces of Me<sub>3</sub>SnC<sub>6</sub>H<sub>5</sub>. <sup>d</sup> Small amount not quantified. <sup>e</sup> 20% *p*-DNB added. <sup>f</sup> Together with traces of phenylDEP. <sup>g</sup> Substrate/Me<sub>3</sub>SnNa = 1/1. <sup>h</sup> Substrate/Me<sub>3</sub>SnNa = 1/5. <sup>i</sup> Together with Me<sub>3</sub>SnC<sub>6</sub>H<sub>5</sub> (**9**, 19%).

the dark (same time period), we found that there was a slow reaction between **4** and **3**, giving a mixture of the monostannylated compound [(2-trimethylstannyl)phenyl] diethyl phosphate (**8**) (12%), traces of **1**, and substantial amounts of starting substrate (entry 2). This reaction was totally inhibited by the addition of *p*-dinitrobenzene (*p*-DNB) (20%), a well-known inhibitor of S<sub>RN</sub>1 reactions,<sup>11</sup> recovering unreacted starting material (entry 3). It should be noted that in the photostimulated reaction, after 90 min, no monosubstitution product **8** was detected. Nevertheless, when the reaction between **4** and **3** was quenched at shorter times (15 min), a mixture of monostannylated compound **8** (39%) and distannylated compound **1** (11%) together with starting material was obtained (entry 4). Under similar conditions, after 5 min irradiation, the reaction led to a mixture of **8** in about 15% yield, traces of **1**, and about 80% of unreacted **4** (entry 5). The yield of **1** progressively increased with time at the expense of **8**, and after 90 min **1** was the only product, with complete consumption of the substrate. These results constitute evidence that **8** is an intermediate in the transformation of **4** into **1**. Also, the formation of **8** indicates that chlorine is the first nucleofuge replaced in the reaction. This is in accord with the fact that chlorobenzene is more reactive than phenyl diethyl phosphate toward **3** in liquid ammonia.<sup>12</sup> The fact that the reaction between **4** and **3** is stimulated by irradiation and that the slow reaction in the dark is suppressed by *p*-DNB indicates the radical-chain character of the substitution process. These results suggest that the reaction occurs by the S<sub>RN</sub>1 mechanism, through two propagation cycles, as sketched in Scheme 1.

The radical anion **8**<sup>•-</sup> may suffer two competing reactions: electron transfer to **4**, which furnishes the monosubstitution product **8** (step 2), or bond fragmentation to expel diethyl phosphate anion, leading to radical **9**<sup>•</sup> (step 1), which ultimately leads to disubstitution product **1**. The formation of **8** as an intermediate in this

**Scheme 1**

reaction indicates that step 2 is faster than step 1 under the conditions employed. In a second propagation cycle, compound **8** is capable of reacting with nucleophile **3**, leading at last to disubstitution product **1**. It should be noted that step 1 is unimolecular but step 2 is bimolecular, depending on the concentration of substrate. To determine if substrate concentration affects the absolute rate of step 2, we carried out a series of reactions with different substrate concentrations using an insufficient amount of **3** (1/1 ratio). Our results confirm that a larger amount of monostannylated product is formed at higher concentration of substrate.<sup>13</sup> Thus, a larger ratio **8**/**1** (13/1) is obtained at higher substrate concentration and this ratio drops to 7/1 and finally to 0/100 as the substrate concentration diminishes (entries 6–8). The fact that compound **8** is not detected at lower concentrations suggests that under these reaction conditions step 1 competes efficiently with step 2. The conditions

(11) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the S<sub>RN</sub>1 Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983.

(12) Unpublished results.

(13) These results are in agreement with those obtained by Bunnett in the reaction between *m*-chloriodobenzene and diethyl phosphite ion: Bunnett, J. F.; Shafer, S. J. *J. Org. Chem.* **1978**, *43*, 1877.

employed in experiment 7 lead to better yields of the monosubstituted compound **8**.<sup>14</sup>

It should be noted that phenyl diethyl phosphate ester (**7**)<sup>15</sup> has been detected in low percentages (ca. 2–4%) in the reactions carried out at short time (entries 4 and 5) and in the dark (entry 2). The presence of **7** is probably due to the hydrogen abstraction reaction by radical **7**<sup>•</sup> from ammonia. Compound **9**,<sup>16</sup> detected in experiments 1 and 9, probably was formed by the reaction of **7** with **3** under photostimulation,<sup>8</sup> as sketched in eq 1.

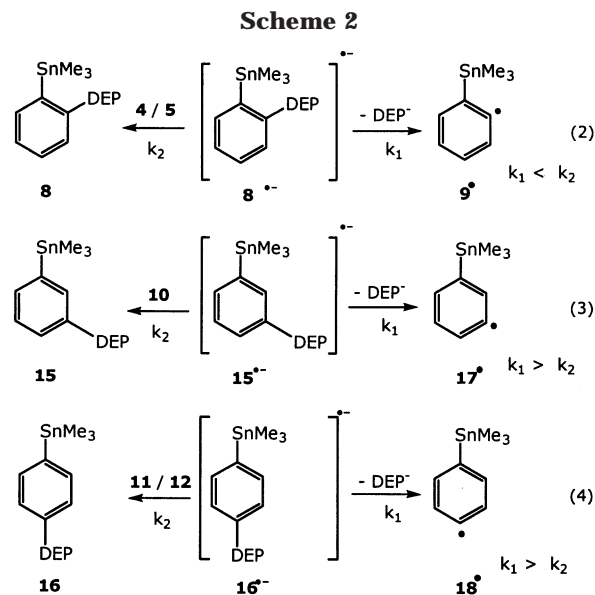
Taking into account our results and with the aim of increasing the yield of **1**, we carried out reactions between **4** and **3** under two different reaction conditions. The results obtained indicate that while an increase in the **3/4** ratio (5/1) did not produce a substantial increment in the yield of **1** (66%) (entry 9), a decrease in the substrate concentration (1.78 mM, **4/3**, 1/2.2 ratio) led to a lower yield of **1** (50%) and to an increase in the yield of compound **9** (19%) (entry 10). The latter result suggests that, at lower concentration, the hydrogen abstraction reaction by the radical **7**<sup>•</sup> from ammonia competes efficiently with the reaction between **7**<sup>•</sup> and anion **3**.

Similar results have been obtained in the reaction of tetraethyl-1,2-phenylene bisphosphate (**5**) with **3**. Thus, there was no reaction in the dark (entry 11), but under irradiation (3.5 h) the disubstitution product **1** was obtained in 67% yield (entry 12). The reaction carried out at shorter time (1.5 h) led to a mixture of monostannylated compound **8** (36%) and distannylated product **1** (21%) (entry 13). While in experiment 13 the presence of **7** (ca. 4%) was detected, in experiment 12 compound **9** was detected in about 3% yield.

Also, experiment 14 shows that an excess of anion **3** did not produce an increment in the percentage of **1** (65%). Taking into account our results, we are able to say that **4** and **5** showed almost the same reaction behavior toward anion **3** in liquid ammonia.

The results obtained in experiments 1 and 12 suggest that **4** is more reactive than **5** toward **3** under the reaction conditions studied. The difference in reactivity is probably due to the fact that chloride is a better leaving group compared with diethyl phosphate anion, thus affecting the rate of formation of radical **7**<sup>•</sup> (Scheme 1).

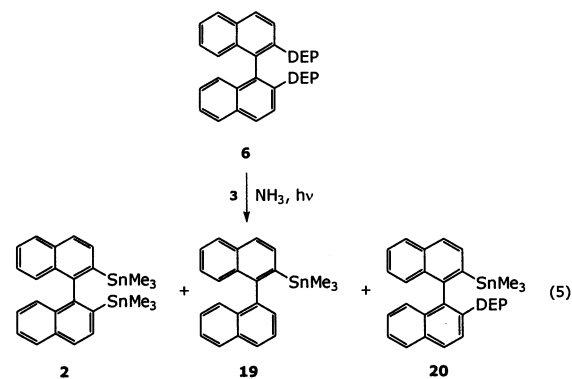
In previous works we have demonstrated that the photostimulated reactions of tetraethyl-1,3-phenylene (**10**) and 1,4-phenylene bisphosphates (**11**) as well as 4-chlorophenyl diethyl phosphate (**12**) with **3** led to the corresponding distannylated products, i.e., 1,3-bis(trimethylstannyl)benzene (**13**) and 1,4-bis(trimethylstannyl)benzene (**14**), in excellent yields (80–97%).<sup>8</sup> In these reactions, monostannylated compounds were not detected even in reactions carried out at short time. Disubstitution without accumulation of monosubstituted product may be attributed to preferential expulsion of the nucleofuge from the intermediate radical anions **15**<sup>•-</sup> and **16**<sup>•-</sup> to form radicals **17**<sup>•</sup> and **18**<sup>•</sup>,



respectively, rather than ET to the corresponding substrate ( $k_2 > k_1$ , Scheme 2). The ET rates are probably similar for eqs 2–4 shown in Scheme 2; therefore, it follows that the intermediacy of a monosubstitution product must be governed by the rate of fragmentation of the intermediate radical anions. The different rates of fragmentation of the 1,2-, 1,3-, and 1,4-trimethylstannyl diethyl phosphate radical anions are probably due to different spin densities at the 2-, 3-, and 4-carbon atoms.<sup>11</sup>

All the experiments performed with 2,2'-bis(diethylphosphoxy)-1,1'-binaphthyl (**6**) are summarized in Table 2.

We have found that there is no reaction between **6** and **3** in the dark (1 h). However, under irradiation in the same time period the disubstitution product 2,2'-bis(trimethylstannyl)-1,1'-binaphthyl (**2**)<sup>17</sup> was obtained in 66% yield together with 2-(trimethylstannyl)-1,1'-binaphthyl (**19**)<sup>18</sup> (14%) and 2-(trimethylstannyl)-2'-(diethylphosphoxy)-1,1'-binaphthyl (**20**) (10%) (entries 1 and 2) (eq 5). These results clearly suggest an  $S_{RN}1$  mechanism.



To determine if compound **20** is an intermediate, we carried out a reaction at short time. In a photostimulated reaction quenched after 15 min was detected **20**

(14) To be used as the starting material in selective substitution reactions (work in progress).

(15) Identified by GC/MS by comparison with an authentic sample synthesized by the method of Kenner.<sup>21</sup>

(16) Identified by GC/MS by comparison with an authentic sample synthesized by known procedures.<sup>8</sup>

(17) Physical characteristics and NMR spectroscopic data are in agreement with those reported in the literature.<sup>2</sup>

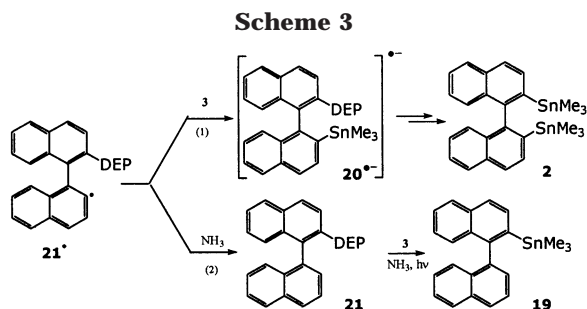
(18) It has been detected and identified by GC/MS. MS ( $m/z$ , relative intensity): 418 (1,  $M^+$ ), 403 (89,  $M - CH_3$ ), 373 (13), 252 (100).



**Table 2. Reaction of 2,2'-Bis(diethylphosphoxy)-1,1'-binaphthyl (6) with Me<sub>3</sub>SnNa in Liquid Ammonia**

entry	3/substrate <sup>a</sup>	conditions (time, h)	2 (%) <sup>b</sup>	19 (%) <sup>b</sup>	20 (%) <sup>b</sup>
1	2.2	dark (1)	0	0	0
2	2.2	hν (1)	66	14	10
3	2.2	hν (0.25)	4	c	32 <sup>d</sup>
4	2.2	hν (4)	69	11	7
5	2.2	hν (7)	74	12	2
6	2.2	hν (10)	76	14	c
7	2.2 <sup>e</sup>	hν (0.5)	7	10	49
8	7	hν (7)	79	7	<2
9	14	hν (7)	82	3	<2

<sup>a</sup> Substrate concentration 2.78 mM, except where stated. <sup>b</sup> Determined by GC. <sup>c</sup> Small amount not quantified. <sup>d</sup> Together with **21** (ca. 8%). <sup>e</sup> Substrate concentration 7.14 mM.



(32%) together with **2** (4%), 2-(diethylphosphoxy)-1,1'-binaphthyl (**21**),<sup>19</sup> (ca. 8%), traces of **19**, and a substantial amount of starting material (entry 3). This result clearly indicates that **20** acts as an intermediate under the reaction conditions studied. It should be noted that, at longer reaction times, the yield of **2** increased at the expense of **20**, while the percentage of **19** remains constant (entries 4–6). The amount of **21** detected in the reaction carried out at short time may result from the reduction of radical **21**<sup>\*</sup>. The presence of compound **19** in all the photostimulated experiments is probably due to the reaction of **21** with **3** under photostimulation as sketched in step 2 of Scheme 3.

Keeping in mind the results obtained in the reaction between **4** and **3** at large substrate concentration and aiming to increase the yield of compound **20**,<sup>14</sup> we carried out experiment 7. Under these reaction conditions compound **20** was formed in 49% yield together with compounds **2** (7%) and **19** (10%).

On the other hand, to improve the yields of disubstitution product **2**, we carried out two reactions employing an excess of anion **3**, as indicated in experiments 8 and 9. Comparison of experiments 5, 8, and 9 suggests that an excess of **3** produces a considerable decrease of **19** together with a slight improvement in the amount of **2**. These results could be explained by considering that once the radical 2-(diethylphosphoxy)-1,1'-binaphthyl (**21**<sup>\*</sup>) is formed, two competitive reactions could take place (Scheme 3). Radical **21**<sup>\*</sup> either reacts with **3**, leading at last to the disubstitution product **2** (step 1), or removes a hydrogen from ammonia, leading to compound **21** (step 2). Step 1 involves a bimolecular reaction whose rate is increased when the reaction is carried out employing an excess of **3**.

All of the aforementioned results constitute evidence that **6** reacts with **3** through an S<sub>RN</sub>1 mechanism in a

(19) It has been detected and identified by GC/MS. MS (*m/z*, relative intensity): 406 (100, M<sup>+</sup>), 378 (9, M - 28), 349 (11), 252 (79).

similar way as **4** and **5** do. Pathways similar to those indicated in Scheme 1 could also be applied for the reaction between **6** and **3**.

## Conclusions

We have developed a new approach for the synthesis of bistannylated aromatic compounds useful as intermediates in the preparation of bidentate Lewis acids. We believe that this is a better and more practical alternative to the existing methodologies of synthesis, since this route proposed leads to the products with good yields via a simple two-step sequence starting from phenols. This route effects, for example, the transformation of **4** and **5** to **1** in an overall yield of 56% (85% in the esterification step and 66% in the substitution step) and the transformation of **6** to **2** in an overall yield of 63% (80% in the esterification step and 79% in the substitution step). It should be noted that Kuivila could not prepare **2** from the more readily accessible binaphthol by applying the Pd-catalyzed coupling of aryl triflates with hexamethyldistannane, even after prolonged heating.<sup>2</sup> Our method also has the advantage that the formation of side products **9** and **19** by the reduction of the radicals is kept to a minimum. It should be pointed out that the separation of substrate **1** from **9** as well as that of **2** from **19** is very difficult. This fact diminishes the yield of purified distannylated products.

The results obtained strongly suggest that the replacement of both nucleofuges in the starting materials goes through an S<sub>RN</sub>1 mechanism and involves the intermediacy of a monosubstitution product.

## 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, that was water-cooled. The reagents were commercially available. 2,2'-Dihydroxy-1,1'-binaphthyl was prepared according to published procedures.<sup>20</sup> Aryl diethyl phosphate esters were prepared by the method of Kenner<sup>21</sup> and characterized by IR and proton NMR spectroscopy.<sup>22</sup> For each compound, the product from at least one reaction was purified and isolated by column chromatography on silica gel, and the IR and NMR spectra as well as MS measurements were determined. To carry out the reactions in the dark, the reaction flask was wrapped with aluminum foil.

**Photostimulated Reaction of 2-Chlorophenyl Diethyl Phosphate (4) with Me<sub>3</sub>SnNa (3).** The reactions were performed by 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 cold finger condenser, a nitrogen inlet, and a magnetic stirrer. Me<sub>3</sub>SnCl (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, **4** (0.132 g, 0.50 mmol) was added and then the mixture was irradiated with stirring, for 1.5 h. The reaction was quenched by adding an aqueous saturated solution of

(20) Vogel's Textbook of Practical Organic Chemistry, 4th ed.; Longman: New York, 1978; p 613.

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

(22) The IR spectra of the esters present characteristic absorptions at 1030, 1155–1164, 1183–1214, and 1265–1274 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra present a double triplet at 1.35–1.51 ppm (<sup>3</sup>J<sub>H,H</sub> = 7.0–7.2 Hz, <sup>4</sup>J<sub>H,P</sub> = 1.1 Hz) and a double quartet at 4.25–4.45 ppm (<sup>3</sup>J<sub>H,H</sub> = 7.0–7.2 Hz, <sup>3</sup>J<sub>H,P</sub> = 5.8–6.2 Hz) as well as the absorption due to the aryl groups.

ammonium chloride, 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<sub>4</sub>. The mixture composition was identified by GC/MS. Product **1** was isolated by TLC chromatography on silica gel (0.111 g, 0.30 mmol, 60%), and its spectroscopic data agreed with those reported in the literature.<sup>1</sup>

**(2-Trimethylstannyl)phenyl Diethyl Phosphate (8).**

Separation of compound **8** from **1** and **4** by careful column chromatography (eluent hexane/ethyl acetate (50/50)) was made feasible from the reaction between **4** and **3** (1/1 ratio) carried out in experiment 6 (Table 1). <sup>119</sup>Sn{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 44.6. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -28.7. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.26 (s, <sup>2</sup>J(H,Sn) = 54.0 Hz, 9 H, SnMe<sub>3</sub>); 1.26 (m, <sup>3</sup>J(H,H) = 7.0 Hz, <sup>4</sup>J(H,P) = 1.0 Hz, 6 H, CH<sub>3</sub>); 4.12 (m, <sup>3</sup>J(H,H) = 7.0 Hz, <sup>3</sup>J(H,P) = 6.0 Hz, 4 H, CH<sub>2</sub>); 7.06 (m, 1 H, Ph); 7.23 (m, 1 H, Ph); 7.35 (m, 2 H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -8.5 (<sup>1</sup>J(C,Sn) = 348/364 Hz, SnCH<sub>3</sub>); 16.5 (<sup>3</sup>J(C,P) = 6.5 Hz, CH<sub>3</sub>); 64.8 (<sup>2</sup>J(C,P) = 6.0 Hz, CH<sub>2</sub>); 118.1 (<sup>3</sup>J(C,Sn) = 16.0 Hz, <sup>4</sup>J(C,P) = 2.0 Hz, C<sub>aryl</sub>); 125.0 (<sup>2</sup>J(C,Sn) = 40 Hz, C<sub>aryl</sub>); 130.5 (C<sub>aryl</sub>); 132.9 (<sup>2</sup>J(C,P) = 11.2 Hz, C<sub>aryl</sub>); 137.2 (<sup>3</sup>J(C,Sn) = 23 Hz, C<sub>aryl</sub>); 156.5 (<sup>3</sup>J(C,P) = 6.5 Hz, C<sub>aryl</sub>). MS (*m/z*, relative intensity): 394 (2, M<sup>+</sup>), 379 (100, M - CH<sub>3</sub>), 351 (17), 337 (4), 323 (82), 307 (39), 293 (34).

**2-(Trimethylstannyl)-2'-(diethylphosphoxy)-1,1'-binaphthyl (20).** Separation of compound **20** from **2** and **6** by careful column chromatography (eluent hexane/ethyl acetate (50/50)) was made feasible from the reaction between **6** and **3** carried

out in experiment 3 (Table 2). <sup>119</sup>Sn{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -27.5. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 43.5. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.0 (s, <sup>2</sup>J(H,Sn) = 55.3/52.8 Hz, 9 H, SnMe<sub>3</sub>); 1.1 (m, <sup>3</sup>J(H,H) = 7.1 Hz, <sup>4</sup>J(H,P) = 1.1 Hz, 3H, CH<sub>3</sub>); 1.26 (m, <sup>3</sup>J(H,H) = 7.1 Hz, <sup>4</sup>J(H,P) = 1.0 Hz, 3H, CH<sub>3</sub>); 3.66 (m, <sup>3</sup>J(H,H) = 7.1 Hz, <sup>3</sup>J(H,P) = 6.0 Hz, 2H, CH<sub>2</sub>); 3.83 (m, <sup>3</sup>J(H,H) = 7.1 Hz, <sup>3</sup>J(H,P) = 5.9 Hz, 2H, CH<sub>2</sub>); 7.44–7.56 (m, 2H, Ph); 7.66–7.71 (m, 2H, Ph); 7.97–8.01 (m, 2H, Ph); 8.11–8.25 (m, 4H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -8.6 (<sup>1</sup>J(C,Sn) = 350.4/333.9 Hz, SnCH<sub>3</sub>); 15.9 (<sup>3</sup>J(C,P) = 7.0 Hz, CH<sub>3</sub>); 16.1 (<sup>3</sup>J(C,P) = 6.5 Hz, CH<sub>3</sub>); 64.4 (<sup>2</sup>J(C,P) = 6.5 Hz, CH<sub>2</sub>); 64.6 (<sup>2</sup>J(C,P) = 6.5 Hz, CH<sub>2</sub>); 119.9 (<sup>4</sup>J(C,P) = 2 Hz, CH<sub>aryl</sub>); 125.8 (CH<sub>aryl</sub>); 126.4 (<sup>4</sup>J(C,P) = 2 Hz, CH<sub>aryl</sub>); 126.8 (CH<sub>aryl</sub>); 127.2 (CH<sub>aryl</sub>); 127.31 (CH<sub>aryl</sub>); 128.1 (CH<sub>aryl</sub>); 128.4 (CH<sub>aryl</sub>); 129.0 (<sup>3</sup>J(C,P) = 8 Hz, C<sub>aryl</sub>); 130.2 (CH<sub>aryl</sub>); 131.4 (C<sub>aryl</sub>); 132.7 (<sup>2</sup>J(C,Sn) = 38 Hz, CH<sub>aryl</sub>); 133.2 (C<sub>aryl</sub>); 133.9 (<sup>4</sup>J(C,Sn) = 8 Hz, C<sub>aryl</sub>); 134.8 (C<sub>aryl</sub>); 141.1 (<sup>3</sup>J(C,Sn) = 29 Hz, C<sub>aryl</sub>); 143.3 (C<sub>aryl</sub>); 147.0 (<sup>2</sup>J(C,P) = 6 Hz, C<sub>aryl</sub>). MS (*m/z*, relative intensity): 570 (3, M<sup>+</sup>), 555 (100, M - CH<sub>3</sub>), 525 (5), 495 (4), 419 (35), 389 (63).

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