JOC Article

Photostimulated Reactions of Vinyl Phosphate Esters with Triorganostannides. Evidence for an $S_{RN}1$ Vinylic Mechanism

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Ketones are converted into vinyl diethyl phosphate esters (VinDEP), which under photostimulation reacted with sodium trimethylstannide (**1**) or sodium triphenylstannide (**2**) in liquid ammonia affording vinylstannanes via a vinylic $S_{RN}1$ mechanism. Thus, (1-phenylvinyl)DEP (**3**), (3,4-dihydro-1-naphthyl)DEP (**7**), (3,4-dihydro-2-naphthyl)DEP (**9**), (*E*)-(1,2-diphenylvinyl)DEP (**12**), (*E*/*Z*)-(1-methyl-2-phenylvinyl)DEP (**14**) and (*E*)-(1-phenyl-2-methylvinyl)DEP (**16**) react with **1** and **2**, under photostimulation, leading to the corresponding substitution products in good to excellent yields (45−89%). On the other hand, there is no reaction between (1-cyclohexenyl)DEP (**5**) or (1-benzylvinyl)DEP (**18**) with either **1** or **2**, under similar conditions. These reactions appear to be strongly dependent on structural features of the vinyl phosphate since only conjugated vinyl phosphates afforded substitution products. These substitution reactions are completely regioselective and stereoconvergent. It seems to be the first example of a vinylic $S_{RN}1$ process involving organotin anions as nucleophiles.

Introduction

Triorganostannyl anions (R_3SnM) have been described in the literature as "supernucleophiles". The displacement of halides and other groups from alkyl, aryl, and vinyl substrates by organotin anions represents one of the most important routes for the formation of new tin−carbon bonds.[1]

Indeed, the reaction of R_3SnM with alkyl derivatives has been extensively studied by several groups.[2−6] On the basis of stereochemical studies, experiments in which intermediates were trapped, and the effect of reaction conditions, three mechanistic pathways have been proposed: (i) direct S_N2 at carbon; (ii) S_N2 at halogen (halogen−metal exchange, HME), and (iii) electron transfer (ET) from R_3SnM in a cage collapse or a chain mechanism ($S_{RN}1$).

On the other hand, the reaction of R_3SnM as nucleophiles with aryl halides has long been known.[7] The mechanisms involved in these reactions strongly depend on the nature of the leaving group, the nucleophile, the solvent, and the reaction conditions. For example, the results obtained by Quintard in the reaction of *p*-chloro- and *p*-fluorotoluenes with Bu_3SnLi in THF suggest that these reactions occur either through a radical or a benzyne mechanism. The relationship of the cine or ipso substitution products depends on whether the reactions were carried out in the dark or under irradiation or in the presence of added substances.[8] Also, a few years ago, Rossi reported that aryl halides react with Ph_3Sn^- and Me_3Sn^- ions in liquid ammonia through an $S_{RN}1$ and/or an HME mechanism leading to the corresponding substitution and/or dehalogenation products, respectively.[9]

Results obtained in our laboratory showed that Ph_3Sn^- ion also reacts with haloarenes in DMSO and acetonitrile as solvents, through an $S_{RN}1$ and/or an HME mechanism. In general, the reactions carried out in DMSO give better yields of substitution product than those carried out in acetonitrile.[10] Recently, we have also described that aryl trimethylammonium salts as well as aryl diethyl phosphate esters react with R_3SnNa in liquid ammonia via an $S_{RN}1$ mechanism leading to the substitution products in good to excellent yields.[11,12]

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[2] (a) Prezzavento, B. A.; Kuivila, H. G. *J. Org. Chem.* **1987**, *52*, 929. (b) Alnajjar, M. S.; Kuivila, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 416. (c) Alnajjar, M. S.; Smith, G. F.; Kuivila, H. G. *J. Org. Chem.* **1984**, *49*, 1271. (d) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. (e) Alnajjar, M.; Kuivila, H. G. *J. Org. Chem.* **1981**, *46*, 1053.

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[4] (a) Lee, K.-W.; San Filippo, J., Jr. *Organometallics* **1983**, *2*, 906. (b) San Filippo, J., Jr.; Silbermann, J. *J. Am. Chem. Soc.* **1982**, *104*, 2831. (c) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

[5] Adcock, W.; Clark, C. I.; Trout, N. A. *J. Org. Chem.* **2001**, *66*, 3362 and references cited therein.

[6] Santiago, A. N.; Toledo, C. A.; Rossi, R. A. *J. Org. Chem.* **2002**, *67*, 2494 and references cited therein.

[7] Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

[8] (a) Quintard, J. P.; Hauvette-Frey, S. *J. Organomet. Chem.* **1978**, *159*, 147. (b) **1976**, *112*, C11.

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

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

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SCHEME 1

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

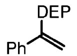
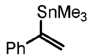
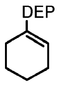
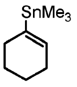
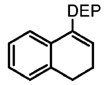
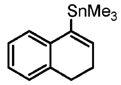
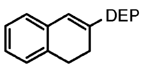
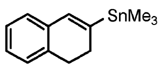
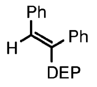
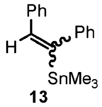
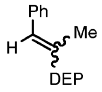
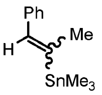
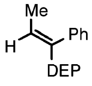
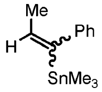
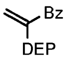
$$(\mathrm{VyX})^{\bullet -} \longrightarrow \mathrm{Vy}^\bullet + \mathrm{X}^- \qquad (2)$$

$$\mathrm{Vy}^\bullet + \mathrm{Nu}^- \longrightarrow (\mathrm{VyNu})^{\bullet -} \qquad (3)$$

$$(\mathrm{VyNu})^{\bullet -} + \mathrm{VyX} \longrightarrow \mathrm{VyNu} + (\mathrm{VyX})^{\bullet -} \qquad (4)$$

$$\mathrm{Vy}^\bullet + \mathrm{SH} \longrightarrow \mathrm{VyH} + \mathrm{S}^\bullet \qquad (5)$$

TABLE 1. Reaction of Vinyl Phosphates with Me_3SnNa in Liquid NH_3[a]

entry	vinylDEP	conditions time (h)	vinyl stannane	yield (%) (*E/Z*)
1	 3	hν, 2	 4	82
2	 5	hν, 5	 6	0
3		hν, 5[b]		0
4	 7	hν, 5	 8	10
5		hν, 5[b]		47
6	 9	hν, 5	 10	4[c]
7		hν, 5[b]		45[d]
8	 12	hν, 3	 13	70 (80/14)
9		dark, 3		6 (89/11)
10		dark, 3[e]		0
11[f]	 14	hν, 2	 15	73 (92/8)
12[g]		hν, 3[e]		60
13[g]		hν, 3		76 (93/7)
14	 16	hν, 3	 17	85 (42/58)
15		hν, 3[e]		22 (42/58)
16	 18	hν, 3		0

[a] Substrate/Me_3SnNa, 1/1.2. [b] Substrate/Me_3SnNa, 1/5. No substitution products were detected without irradiation, unless where it is stated. [c] Together with **11**, ca. 2%. [d] Together with **11**, ca. 15%. [e] 20% *p*-DNB added. [f] *E*/*Z*, 39/61. [g] *E*/*Z*, 76/24.

There are several antecedents in the literature about the synthesis of vinylstannanes by the reaction of R_3Sn^- ions with vinyl compounds supporting different leaving groups. Thus, Piers has reported that the reaction of β-iodo enones with Me_3SnLi in THF resulted in the formation of moderate amounts of the corresponding substitution products although the results were not very reproducible. Nevertheless, when these reactions were carried out with lithium phenylthio(trimethylstannyl)cuprate instead of Me_3SnLi, the yield of substitution products was substantially increased.[13] Stannyl cuprates also react with β-X-α,β-unsaturated esters (X = Cl, I, OTos, OTf, SPh)[14,15] as well as with vinyl iodides and vinyl triflates[16] to give vinylstannanes in good to excellent yields. All of these reactions may be considered either as nucleophilic substitutions or addition–elimination reactions. It should be mentioned that Oshima[16] has reported that the reaction of vinyl phosphates with tin anions ($R_3SnAlEt_3$) in the presence of $Pd(PPh_3)_4$ catalyst gave no desired vinylstannane. We now report the results obtained and the mechanistic aspects of the reaction of Me_3SnNa (**1**) and Ph_3SnNa (**2**) with vinyl diethyl phosphate esters (VinDEP)[17] in liquid ammonia. We have found that an $S_{RN}1$ reaction does indeed occur under photostimulation.

Although rather scanty, there are antecedents in the literature concerning vinyl substitutions by the $S_{RN}1$ mechanism, in which a carbon nucleophile reacts with a halovinyl derivative.[18] The proposed mechanism is a chain process in which radicals and radical anions are involved as intermediates, as is illustrated in Scheme 1.

In a few systems, this chain process is initiated by spontaneous ET from the nucleophile to the substrate forming the vinylic radical anion (eq 1). Stimulation by UV light or by Fe^{2+} has been recently applied in vinylic $S_{RN}1$ reactions.[18] It should be noted that the coupling with the nucleophile (eq 3) is not the only reaction that vinyl radicals can undergo: hydrogen atom transfer from the solvent is one of the most important side reactions (eq 5). This competitive reaction is reduced by using liquid ammonia as solvent, which is a poor hydrogen atom donor.[19]

As far as we know, our results are the first example of $S_{RN}1$ vinylic substitution with organotin anions as nucleophiles.

Results and Discussion

Reactions with Me_3SnNa (1). The results obtained are summarized in Table 1.

We have found that under irradiation (1-phenylvinyl)-DEP (**3**)[20] reacts with **1** to give the corresponding

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(13) Piers, E.; Morton, H. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1033.

(14) Piers, E.; Tse, L. A. *Tetrahedron Lett.* **1984**, *25*, 3155.

(15) Seitz, D. E.; Lee, S.-H. *Tetrahedron Lett.* **1981**, *22*, 4909.

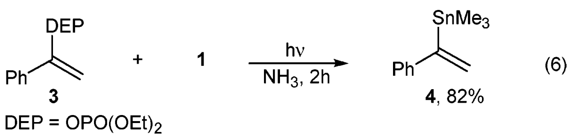
(16) Matsubara, S.; Hibino, J.-I; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Organomet. Chem.* **1985**, *285*, 163.

(17) Vinyl phosphates were prepared from the corresponding carbonyl compounds by trapping the enolate with diethyl chlorophosphate according to: Ireland, R. E.; Pfister, G. *Tetrahedron Lett.* **1969**, 2145. The IR spectra of the esters (as films) present characteristic absorption at 1030, 1155–1164, 1183–1214, and 1265–1274 cm^{-1}.

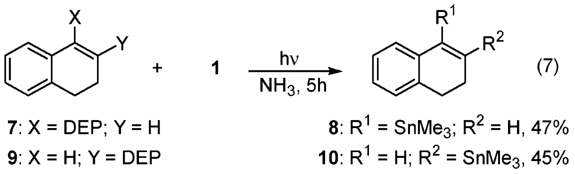
(18) (a) Annunziata, A.; Galli, C.; Gentili, P.; Guarnieri, A.; Beit-Yannai, M.; Rappoport, Z. *Eur. J. Org. Chem.* **2002**, 2136 and references cited therein. (b) Santiago, A. N.; Lassaga, G.; Rappoport, Z.; Rossi, R. A. *J. Org. Chem.* **1996**, *61*, 1125.

(19) Rossi, R. A.; Pierini, A. B.; Santiago, A.N. *Aromatic Substitution by the $S_{RN}1$ Reaction*; *Organic Reactions*; Paquette, L.A., Bittman, R., Eds.; John Wiley & Sons: New York, 1999; Vol. 54, p 1.

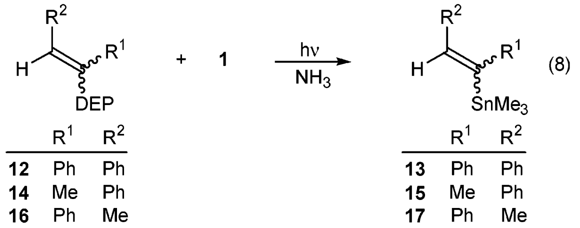
substitution product, 1-phenyl-1-(trimethylstannyl)ethene (**4**) in 82% yield (2 h)[21] (eq 6). There is no reaction without photostimulation (in the dark) and the substrate **3** was recovered unchanged (Table 1, entry 1).



On the other hand, (1-cyclohexenyl)DEP (**5**)[20] is unreactive toward **1** even after 5 h under irradiation in the presence of an excess of **1**. No substitution product, i.e., 1-(trimethylstannyl) cyclohexene (**6**), was detected, and the starting substrate was almost completely recovered (Table 1, entries 2 and 3). Otherwise, the photostimulated reaction of both (3,4-dihydro-1-naphthyl)DEP (**7**)[22] and (3,4-dihydro-2-naphthyl)DEP (**9**)[22] with **1** led to the corresponding substitution products, i.e., 3,4-dihydro-1-(trimethylstannyl)naphthalene (**8**)[23] and 3,4-dihydro-2-(trimethylstannyl)naphthalene (**10**),[23] although in very low yields (10% and 4%, respectively). Considerable amounts of unreacted precursors were present in each case. It should be noted that an increase in the **1**/**7** and **1**/**9** ratio (5/1) produced a substantial increment on the yield of **8** (47%) and **10** (45%) (eq 7) (Table 1, entries 4−7). In experiments 6 and 7 (Table 1), together with the substitution product **10**, the reduction product 3,4-dihydronaphthalene (**11**) was detected in ca. 2% and 15% yields, respectively. When these reactions were carried out in the dark neither substitution nor reduction products were detected. The presence of **11** is probably due to the hydrogen abstraction reaction by the radical intermediate from ammonia (eq 5).



We have also found that there was a slow reaction between (*E*)-(1,2-diphenylvinyl)DEP (**12**)[20] and **1** in the dark, giving the substitution product 1,2-diphenyl-1-(trimethylstannyl)ethene (**13**, *E*/*Z*, 89/11) in 6% yield (3 h).[21] This reaction was totally inhibited by the addition of *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions.[12] On the other hand, when the reaction was carried out under irradiation, the yield of **13** (as a mixture of isomers *E*/*Z*, 86/14) was substantially increased to 70% in the same time period (eq 8) (Table 1, entries 8−10). The slow dark reaction inhibited by the addition of *p*-DNB indicates that a spontaneous ET from the nucleophile to the substrate occurs which is stimulated by irradiation.



Also, the photostimulated reactions of **1** with (*E*/*Z*)-(1-methyl-2-phenylvinyl)DEP (**14**)[22] and (*E*)-(1-phenyl-2-methylvinyl)DEP (**16**)[20] yield the corresponding substitution products 1-phenyl-2-(trimethylstannyl)propene (**15**) in 73% yield (*E*/*Z*, 92/8; 2 h)[24] and 1-phenyl-1-(trimethylstannyl)propene (**17**) in 85% yield (*E*/*Z*, 42/58; 2 h),[23] respectively (eq 8). It should also be noted that both reactions are partially inhibited by the addition of *p*-DNB (20%) and that no substitution product is formed in the dark (Table 1, entries 11−15). To analyze the stereochemistry of these reactions, we carried out similar photostimulated reactions starting from different *E*/*Z* (39/61; 76/24) mixtures of compound **14**. In all the reactions, similar *E*/*Z*-mixtures (within 2%) of product **15** were obtained independently of the starting substrate configuration; i.e., the reaction is stereoconvergent (entries 11 and 13). It should be noted that in both experiments 11 and 13 the unreacted substrate **14** was recovered with unchanged configuration, showing that *E* and *Z* isomers are stable to isomerization under the reaction conditions. Additional checks confirmed that product **15** undergoes no isomerization under the reaction conditions. Thus, after irradiation (2 h), but in the absence of the organotin anion, different (*E*,*Z*)-**15** mixtures were recovered unchanged. We conclude that the loss of configuration must take place during the substitution process. The stereochemistry of the products probably depends on the structure of the vinyl radical intermediate.[25] It seems that the final *E*/*Z* mixtures depend on the nature of the *β*-substituents. Thus, compounds **12** and **14**, supporting a Ph group on the *β*-carbon, led to higher yields of (*E*) isomers, whereas compound **16**, supporting a *β*-Me group, led to higher yields of (*Z*) isomer.

When we carried out the reaction of (1-benzylvinyl)-DEP (**18**)[26] with **1**, no substitution product was detected even after 5 h under irradiation, and the starting substrate was almost completely recovered (Table 1, entry 16).

From the above-mentioned results it is evident that, in the systems studied, the substitution products were formed through an $S_{RN}1$ mechanism: (i) the reactions did not take place in the dark and (ii) the rate of the reactions were significantly reduced when *p*-DNB was added. The occurrence of the $S_{RN}1$ mechanism appears to be dependent on some structural features of the starting substrate.

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[20] Spectroscopic data were in agreement with those reported by: Borowitz, I. J.; Firstenberg, S.; Casper, E. W. R.; Crouch, R. K. *J. Org. Chem.* **1971**, *36*, 3282. It was also characterized by ^{13}C NMR and MS spectra.

[21] NMR spectroscopic data were in agreement with those reported by: Cochran, J. C.; Phillips, H. K.; Tom, S.; Hurd, A. R.; Bronk, B. S. *Organometallics* **1994**, *13*, 947.

[22] Characterized by its IR, ^{1}H, ^{13}C, ^{31}P NMR, and MS spectra.

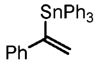
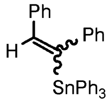
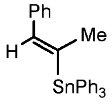
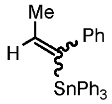
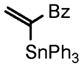
[23] Characterized by its ^{1}H, ^{13}C, ^{119}Sn NMR, and MS spectra.

[24] NMR spectroscopic data are in agreement with those reported by: Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1983**, *252*, 47. It was also characterized by MS spectra.

[25] Galli, C.; Gentili, P.; Guarnieri, A.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 8878.

[26] ^{1}H NMR spectroscopic data were in agreement with those reported by: Kosugi, M.; Miyajima, Y.; Nakanishi, H.; Sano, H.; Migita, T. *Bull. Chem. Soc. Japan* **1989**, *62*, 3383. It was also characterized by ^{13}C, ^{31}P NMR and MS spectra.

TABLE 2. Reaction of Vinyl Phosphates with Ph_3SnNa in Liquid NH_3[a]

entry	VinylDEP	conditions time (h)	vinyl stannane	yield (%) (E/Z)
1	**3**	hν, 2	 **19**	82
3	**12**	hν, 3	 **20**	86 (81/19)
5[b]	**14**	hν, 3	 **21**	78 (100/0)
7	**16**	hν, 3	 **22**	89 (34/66)
9	**18**	hν, 3	 **23**	0

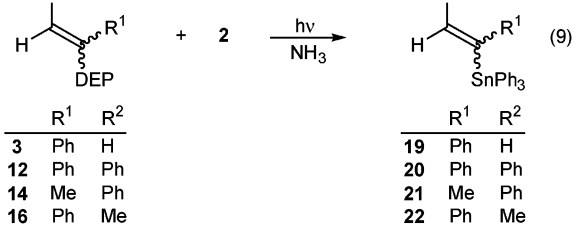
[a] Substrate/Ph_3SnNa, 1/1.2. [b] *E*/*Z*, 76/24.

Thus, both compounds **5** and **18**, which do not react with **1** under photostimulation, are unconjugated vinyl phosphates whereas all the conjugated vinyl systems studied afford the substitution products in good to excellent yields. Probably, this different reactivity could be due to the fact that a conjugated vinyl phosphate is easier to reduce than an unconjugated one, favoring the ET from the nucleophile **1** to the substrate (eq 1, Scheme 1).

Reactions with Ph_3SnNa (2). To analyze the effect of the triorganostannyl anion on the reactivity with vinyl phosphates, we studied the reactions of **2** with different substrates in liquid ammonia.

In Table 2 it can be seen that the photostimulated reactions of **3**, **12**, **14**, and **16** with **2** gave the expected stannylated derivatives. Thus, 1-phenyl-1-(triphenylstannyl)ethene (**19**),[27] 1,2-diphenyl-1-(triphenylstannyl)ethene (**20**, *E*/*Z*, 81/19),[23] 1-phenyl-2-(triphenylstannyl)propene (**21**, *E*/*Z*, 100/0),[23] and 1-phenyl-1-(triphenylstannyl)-propene (**22**, *E*/*Z*, 34/66)[23] were obtained in 82, 86, 78, and 89% yields, respectively (eq 9). The substitution products were easily detected by GC−MS analysis.

When these reactions were carried out in the dark no substitution product was detected. All of these observations strongly suggest that these reactions also take place through an $S_{RN}1$ mechanism.



(9)

Again, the stereochemical results show that these reactions are stereoconvergent. Once more, β-Ph vinyl phosphates **12** and **14** afforded mixtures of substitution products showing a high excess of (*E*) over (*Z*) isomer whereas β-Me vinyl phosphate **16** led to a mixture enriched on (*Z*) isomer.

On the other hand, results similar to those obtained in the reaction between compound **18** and **1** were obtained in the reaction of **18** with **2**. Thus, there is no reaction and **18** was recovered unchanged under these reaction conditions.

In all cases, the NMR spectra of the reaction mixtures showed no signals corresponding to the other possible isomers, thus indicating the complete regioselectivity of these substitution reactions. The stereochemistry of vinyltins was defined on the basis of ^{13}C and ^{1}H chemical shifts and vicinal $^{1}H-^{119}Sn$ and $^{13}C-^{119}Sn$ couplings, which show a sensitive dependence on dihedral angle.[28,29]

Conclusions

Recently, we have demonstrated that the diethyl phosphate group can act as a nucleofuge in the reaction of aryl phosphate esters with trimethyl- and triphenyltin anions in liquid ammonia under irradiation and that these reactions take place through an $S_{RN}1$ mechanism.[12] Our present results confirm that vinyl phosphate esters also react with these tin anions in liquid ammonia by a comparable substitution mechanism. We have found that these vinylic $S_{RN}1$ reactions strongly depend on structural features of the vinyl phosphate. Thus, only conjugated vinyl phosphates afforded the substitution product by $S_{RN}1$. It should be mentioned that similar results have been found by Galli and Rappoport in the reaction of vinyl halides with carbon nucleophiles.[18a] Nevertheless, they have also found that those reactions are only limited to conjugated vinyl halides lacking either a vinylic or allylic hydrogen. Thus, vinyl halides having β-vinylic hydrogen undergo substitution by an elimination−addition route, whereas vinylic halides supporting allylic or vinylic hydrogen(s) give substituted allene. In our reactions we have not found these limitations.

The reactions informed here would be of interest not only from a mechanistic point of view but also as an alternative route[14,16,30] for the synthesis of vinylstannanes starting from unsymmetrical ketones. The method involves the regioselective conversion of the starting ketone into the corresponding kinetic or thermodynamic phosphate ester and treatment of the latter with tin anions in liquid ammonia.

Work is in progress to determine the scope of these reactions.

Experimental Section

General Methods. Irradiation was conducted in a reactor made of Pyrex, equipped with four 250 W UV lamps emitting

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[27] NMR spectroscopic data were in agreement with those reported by: Nonaka, T.; Okuda, Y.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1986**, *51*, 4716. It was also characterized by MS spectra.

[28] Betzer, J.-F.; Le Ménez, P.; Prunet, J.; Brion, J.-D.; Ardisson, J.; Pancrazi, A. *Synlett* **2002**, 1.

[29] Mitchell T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1986**, *304*, 257.

[30] Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Clan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277.

maximally at 350 nm, water-cooled. To carry out the reactions in the dark, the reaction flask was wrapped with aluminum foil.

^{1}H, ^{13}C, ^{119}Sn, and ^{31}P NMR spectra were recorded in $CDCl_3$ on a 300 MHz spectrometer and are referenced to TMS (^{1}H and ^{13}C) or Me_4Sn (^{119}Sn) or (^{31}P). Mass spectra were recorded by GC/MS.

General Procedure for Irradiated Reactions. A 125 mL portion of sodium-dried ammonia was condensed into a three-necked, round-bottomed Pyrex flask equipped with a coldfinger condenser, a nitrogen inlet, and a magnetic stirrer. Me_3SnCl (1.1 mmol) and Na metal (2.60 mg atom) were added. When the blue color disappeared, 0.90 mmol of vinyl phosphate was added and then the mixture irradiated with stirring as indicated in Tables 1 and 2. The reaction was quenched by addition of ammonium chloride, and ammonia was allowed to evaporate. The residue was treated with water and then extracted with ether. The vinyl trimethyltin derivatives were quantified by GC using the external standard method. On the other hand, vinyltriphenyltin products were quantified by isolation and weighing.

All the products were purified by column chromatography on silica gel treated with triethylamine in order to avoid destannylation of vinylstannanes.

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Supporting Information Available: Tables containing ^{1}H, ^{13}C, and ^{31}P NMR data and MS data of new vinyl diethyl phosphates; ^{1}H, ^{13}C, and ^{119}Sn NMR data and MS data of new organotin derivatives. ^{13}C NMR spectra of vinyl diethyl phosphates and vinyltin derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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