# Sequential Reactions of Trimethylstannyl Anions with Vinyl Chlorides and Dichlorides by the $S_{RN}1$ Mechanism Followed by Palladium-Catalyzed Cross-Coupling Processes

Eduardo F. Córsico and Roberto A. Rossi*

*INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas,*
*Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina*

*rossi@dqo.fcq.unc.edu.ar*

*Received April 28, 2004*

The reactions of trimethylstannyl ions ($Me_3Sn^-$) with vinyl chlorides in liquid ammonia give good yields of vinylstannanes. Some of them react in the dark, and others need light stimulation to react. The fact that these reactions are inhibited by radical and radical anion traps shows that they occur by the $S_{RN}1$ mechanism. When the reaction takes place with 1,1-dichloro-1-alkenes, monosubstitution reduced products are formed in an *E*/*Z* mixture. The efficient synthesis of triarylolefins by Pd(0)-catalyzed cross-coupling reactions of vinylstannanes with several iodoarenes is reported. Similar yields were obtained in one-pot-type reactions.

## Introduction

The first report suggesting the occurrence of a vinylic $S_{RN}1$ route was the photostimulated reaction of acetone enolate ion with $\beta$-bromostyrene in liquid ammonia.[1] Many years later, new evidence has indicated competition with an ionic elimination−addition pathway, particularly with basic enolate ions as nucleophiles in DMSO.[2] Unambiguous vinylic $S_{RN}1$ substitutions by carbanions are known.[3,4] The $S_{RN}1$ mechanism has been proposed for the photoinduced catalytic carbonylation of vinyl bromides and chlorides with $NaCo(CO)_4$ under PTC conditions at atmospheric pressure, which constitutes a very interesting synthesis of $\alpha,\beta$-unsaturated carboxylic acids.[5] Benzenethiolate ions also react with vinyl halides by the $S_{RN}1$ mechanism.[1,3c] The reaction of organostannyl anions with vinyl halides is known, but no mechanistic studies have been done to know if these reactions occur by the $S_{RN}1$ mechanism.[6,7] On the other hand, this is the mechanism recently proposed for the photostimulated reaction of vinyl phosphate esters with $Me_3Sn^-$ ions to afford vinyltrimethylstannanes in liquid ammonia.[8]

It is known that the photostimulated reaction of trimethylstannyl ions ($Me_3Sn^-$) with several mono-, di-, and trichloroarenes in liquid ammonia afforded substitution products in very good to excellent yields by the $S_{RN}1$ mechanism.[9] The arylstannanes thus obtained react with aryl halides to give the cross-coupling products.[10,11] These reactions can be performed by two consecutive steps, or can be done in one-pot-type reactions.[10]

Now we report the reaction of vinyl chlorides with $Me_3Sn^-$ ions in liquid ammonia by the $S_{RN}1$ mechanism to obtain vinylstannanes. In these experimental conditions, Mitchell reported the reaction of 1,2-dibromostilbene with $NaSnMe_3$, obtaining after 1 h hexamethylditin and diphenylacetylene. No light was used to induce the reaction.[6]

The $S_{RN}1$ reaction is a process through which a nucleophilic substitution is obtained.[12] The scope of the process has considerably increased, and nowadays it is an important synthetic possibility to achieve substitution of different substrates. These reactions are an alternative route to the synthesis of stannanes, avoiding the use of Grignard reagents or organolithium compounds. The mechanism is a chain process, whose main steps are presented in Scheme 1.

This chain process requires an initiation step. In a few systems, spontaneous electron transfer (ET) from the

---

[1] Bunnet, J. F.; Creary, X.; Sundberg, J. E. *J. Org. Chem.* **1976**, *41*, 1707−1709.

[2] Galli, C.; Gentili, P.; Rappoport, Z. *J. Org. Chem.* **1994**, *59*, 6786−6795.

[3] (a) Amatore, C.; Galli, C.; Gentili, P.; Guarnieri, A.; Schottland, E.; Rapporport, Z. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2341−2350. (b) Santiago, A. N.; Rossi, R. A.; Lassaga, G.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 1125−1128. (c) Annunziata, H.; Galli, C.; Gentili, P.; Guarnieri, A.; Beit Yannai, M.; Rappoport, Z. *Eur. J. Org. Chem.* **2002**, 2136−2143.

[4] For a discussion of different mechanisms for vinylic substitutions, see: Galli, C.; Rappoport, Z. *Acc. Chem. Res.* **2003**, *36*, 580−587.

[5] (a) Brunet, J. J.; Sidot, C.; Caubere, P. *J. Org. Chem.* **1983**, *48*, 1166−1171. (b) Marchal, J.; Bodiguel, J.; Fort, Y.; Caubere, P. *J. Org. Chem.* **1995**, *60*, 8336−8340.

[6] Mitchell, T. N.; Reimann, W. *Organometallics* **1986**, *5*, 1991−1997.

[7] Mitchell, T. N.; Böttcher, K.; Bleckmann, P.; Costisella, B.; Schwittek, C.; Nettelbeck, C. *Eur. J. Org. Chem.* **1999**, *2413*, 3−2417.

[8] Chopa, A. B.; Dorn, V. B.; Badajoz, M. A.; Lockhart, M. T. *J. Org. Chem.* **2004**, *69*, 3801−3805.

[9] Córsico, E. F.; Rossi, R. A. *Synlett* **2000**, 227−229.

[10] Córsico, E. F.; Rossi, R. A. *Synlett* **2000**, 230−232.

[11] Córsico, E. F.; Rossi, R. A. *J. Org. Chem.* **2002**, *67*, 3311−3317.

[12] For reviews, see: (a) Rossi, R. A.; Pierini A. B.; Peñéñory, A. B. Recent Advances in the $S_{RN}1$ Reaction of Organic Halides. In *The Chemistry of Functional Groups*; Patai S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1995; Suppl. D2, Chapter 24, p 1395. (b) 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, Inc.: New York, 1999; Vol. 54, p 1. (c) Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. *Chem. Rev.* **2003**, *103*, 71−168.

10.1021/jo049287z CCC: $27.50

**SCHEME 1**

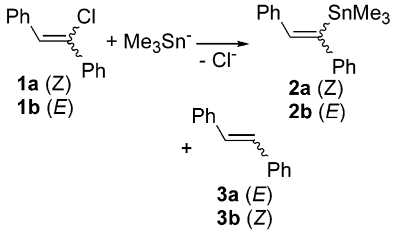
$$(RX)^{\bullet -} \longrightarrow R^{\bullet} + X^{-}$$
$$R^{\bullet} + Nu^{-} \longrightarrow (RNu)^{\bullet -}$$
$$(RNu)^{\bullet -} + RX \longrightarrow (RX)^{\bullet -} + RNu$$

nucleophile to the substrate has been observed. When the ET does not occur spontaneously, it can be induced by light stimulation.[12]

The palladium-catalyzed cross-coupling reaction of organostannanes with electrophiles (Stille reaction)[13] is a widely employed process for generating carbon−carbon bonds. This coupling procedure has become a synthetically important and versatile method because of the tolerance to many functional groups and the stability of the stannanes. Triarylolefins have molecular-electronics applications and biological activities.[14] These properties convert them in an important family of compounds for synthetic chemists, and this is the reason to search different routes to synthesize this type of structure. These compounds can be prepared by different reactions, such as McMurry coupling,[15] Wittig-type reactions,[16] Stille reaction of 1,1-dibromo-1-alkenes,[17] among others. Recently the synthesis of 1,1-diarylethylenes from α-stannyl-*β*-silylstyrene has been reported.[18]

## Results and Discussion

**$S_{RN}1$ Reactions.** There is a fast reaction (4 min) of (*Z*)-1-chloro-1,2-diphenylethene (**1a**) with $Me_3Sn^-$ ions in the dark to afford the substitution product trimethyl((*Z*)-1,2-diphenylvinyl)stannane (**2a**) in 87% yield and 9% of the reduction product (*E*)-1,2-diphenylethene (**3a**) (Table 1, experiment 1). When the concentration ratio $Me_3Sn^-$/**1a** is less than ca. 4, lower yields of **2a** are obtained. A lower yield of substitution product **2a** (45% yield) is obtained when this reaction is carried out with the addition of *p*-dinitrobenzene (*p*-DNB), a well-known radical anion trap, and the reduction product **3a** is formed in 40% yield, indicating a partial inhibition. Finally, with the addition of di-*tert*-butyl nitroxide (DTBN) as radical trap, no substitution product **2a** was formed; only **3a** was afforded in 89% yield (eq 1) (experiments 1−3, Table 1).



(1)

**TABLE 1. Reactions of Vinyl Mono- and Dichlorides with $Me_3Sn^-$ in Liquid Ammonia**[a]

| entry | substrate (amt, mmol) | amt of $Me_3Sn^-$, mmol | conditions (time, min) | $[Cl^-]$, % | products (yield, %) |
|---|---|---|---|---|---|
| 1 | **1a** (0.13) | 0.61 | dark (4) | 99 | **2a** (87), **3a** (9) |
| 2 | **1a** (0.17) | 0.74 | dark (4)[b] | 96 | **2a** (45), **3a** (40) |
| 3 | **1a** (0.15) | 0.63 | dark (4)[c] | 100 | **2a** (0), **3a** (100) |
| 4 | **1b** (0.18) | 0.74 | dark (10) | 95 | **2b** (92), **3b** (15) |
| 5 | **1b** (0.10) | 0.42 | dark (10)[b] | 94 | **2b** (35), **3b** (47) |
| 6 | **1b** (0.11) | 0.44 | dark (10)[c] | 99 | **2b** (0), **3b** (99) |
| 7 | **4a** (0.15) | 0.70 | dark (60) | 0 | **5a** (0) |
| 8 | **4a** (0.18) | 0.85 | *hν* (60) | 98 | **5a** (92) |
| 9 | **4b** (0.16) | 0.69 | dark (60) | 95 | **5b** (88) |
| 10 | **4b** (0.12) | 0.55 | dark (60)[b] | 0 | **5b** (0) |
| 11 | **4c** (0.11) | 0.80 | dark (60) | 28 | **5c** (20) |
| 12 | **4c** (0.15) | 1.20 | dark (60)[b] | 7 | **5c** (<5) |
| 13 | **4c** (0.50) | 2.00 | *hν* (60) | 96 | **5c** (91) |

[a] The reaction was carried out in 250 mL of dry liquid ammonia under a nitrogen atmosphere. The chlorides were determined potentiometrically and for substrates **4** were considered two chlorines. The products were determined by GLC using the internal standard method. [b] *p*-DNB (20 mol %) was added. [c] DTBN (5 mol %) was added.

Similar results were found with (*E*)-1-chloro-1,2-diphenylethene (**1b**); there is a fast reaction in the dark to afford trimethyl((*E*)-1,2-diphenylvinyl)stannane (**2b**) in high yield and a low yield of (*Z*)-1,2-diphenylethene (**3b**). With *p*-DNB and DTBN there is a decrease of **2b** and an increase in the yield of **3b** (eq 1) (experiments 4−6, Table 1).

The facts that the reactions are partially inhibited by *p*-DNB and totally inhibited by DTBN indicate that the products **2** are formed by the $S_{RN}1$ mechanism. There is another competing reaction to yield the reduction products **3**, the halogen−metal exchange (HME), to furnish the vinyl anion, which is protonated by liquid ammonia very fast. There is precedent that the reaction of iodo or bromo arenes with $Me_3Sn^-$ ions in liquid ammonia by HME affords only the reduction products.[19]

Cochran et al. reported the synthesis of **2a** by AIBN-catalyzed hydrostannation of diphenylacetylene with trimethylstannane at 70 °C overnight. The product was obtained in 55% yield.[20] The isomer **2b** was obtained by palladium(0)-catalyzed hydrostannation of diphenylacetylene with trimethylstannane in THF with a 68% yield of crude product.[20]

It is known that some vinyl radical intermediates are configurationally unstable radicals, and from an *E* or *Z* isomer, the $S_{RN}1$ products yield a mixture of *E* and *Z* isomers. For instance, in the reaction of *p*-anisyldiphenylvinyl bromide with $^-CH_2COBu$-*t* ions in DMSO, complete loss of the original stereochemistry of the *E* and *Z* bromide isomers is observed in the substituted and dehalogenated reduced products.[21] The stereoconvergence observed indicates that the intermediate vinyl radical has

---

[13] For reviews, see: (a) Farina, V.; Krishnamurthy, V.; Scott, W. J. The Stille Reaction. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley & Sons, Inc.: New York, 1997; Vol. 50, p 1. (b) Mitchell, T. N. In *Metal Catalysed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1998; p 167.

[14] (a) Van Ginkel, F. I. M.; Cornelisse, J.; Lodder, G. *J. Am. Chem. Soc.* **1991**, *113*, 4261−4272. (b) Jung, S. H.; Choi, J. H.; Kwon, S. K.; Cho, W. J.; Ha, C. S. *Thin Solid Films* **2000**, *363*, 160−162. (c) Doré, J. C.; Gilbert, J.; Bignon, E.; de Paulet, A. C.; Ojasoo, T.; Pons, M.; Raynaud J. P.; Miquel J. F. *J. Med. Chem.* **1992**, *35*, 573−583. (d) Singh, S.; Meyer, K. L.; Magarian, R. A. *Biorg. Chem.* **1996**, *24*, 81−94.

[15] McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513−1524.

[16] Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863−927.

[17] Shen, W.; Wang, L. *J. Org. Chem.* **1999**, *64*, 8873−8879.

[18] Belema, M.; Nguyen, V. N.; Zusi, F. C. *Tetrahedron Lett.* **2004**, *45*, 1693−1697.

[19] Yammal, C. C.; Podesta, J. C.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 5720−5725.

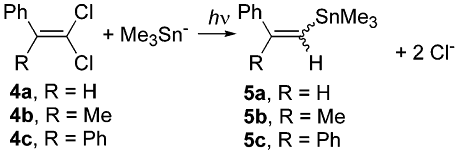
[20] Cochran, J. C.; Phillips, H. K.; Tom, S.; Hurd, A. R.; Bronk, B. S. *Organometallics* **1994**, *13*, 947−953.

[21] Galli, C.; Gentili, P.; Guarnieri, A. Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 8878−8884.

either a linear sp or an "average linear" structure due to a rapidly interconverting $E/Z$ mixture of $sp^2$ bent radicals. Theoretical calculations of some α-substituted vinyl radicals indicate that, for $\pi$-type substituents, the vinyl radicals are linear, meanwhile for $\sigma$-type substituents, the radicals are bent, and the calculated inversion barrier for bent vinyl radicals is 3−20 kcal/mol.[22]

The reactions of **1a** and **1b** with $Me_3Sn^-$ ions afford only one isomer, with the same configuration as the starting vinyl chlorides, which indicates a slower inversion of the vinyl radical intermediate than the coupling reaction with the nucleophile.

Different results were obtained with 1,1-dichloro-1-alkenes (eq 2).



(2)

There is no substitution product in the reaction of 1-(2,2-dichlorovinyl)benzene (**4a**) with $Me_3Sn^-$ ions in dark conditions, but the photostimulated reaction renders a mixture of $E$ and $Z$ isomers of $\beta$-(trimethylstannyl)-styrene (**5a**) (yield 92%, $E/Z = 3/1$, experiments 7 and 8, Table 1). When Cochran et al. carried out the reaction with ($Z$)-$\beta$-bromostyrene, converted this bromide to the Grignard reagent, and coupled it with chlorotrimethylstannane, a 64% yield of **5a** ($E/Z = 1/4$) was obtained. It is also reported that the AIBN-catalyzed reaction between trimethylstannane and phenylacetylene gave **5a** as an $E/Z$ mixture ($E/Z = 14/1$) (yield 42%).[20]

The reaction of 1-(1,1-dichloroprop-1-en-2-yl)benzene (**4b**) in dark conditions afforded trimethyl-(2-phenylprop-1-enyl)stannane (**5b**) in 88% yield ($E/Z = 1/1.3$). No reaction was observed when $p$-DNB was added (experiments 9 and 10, Table 1). The ($E$)-stannane has also been obtained from a Grignard solution (prepared from the vinyl bromide and magnesium turnings in THF) and the addition of chlorotrimethylstannane. The yield was 83%, with a 15% yield of the $Z$ isomer.[23] In another report, the $E$ isomer has been prepared by a procedure which is based on the zirconium-catalyzed methylalumination of phenylacetylene followed by the addition of trimethyltin chloride as electrophile. The yield was 54% with high regio- and stereoisomeric purities.[24]

The reaction of 1,1-dichloro-2,2-diphenylethene (**4c**) with $Me_3Sn^-$ affords a 20% yield of trimethyl(2,2-diphenylvinyl)stannane (**5c**) in dark conditions. This reaction is inhibited by $p$-DNB, indicating an $S_{RN}1$ reaction. Under irradiation, the yield of **5c** increases to 91% (experiments 11−13, Table 1). The same product has been prepared by Grignard coupling between 2-bromo-1,1-diphenylethene and chlorotrimethylstannane. No yield was reported.[20]

It is concluded that, with 1,1-dichloro-1-alkenes as substrates, we obtained only monosubstituted reduced stannanes. In these cases, the coupling of $Me_3Sn^-$ ion with the monosubstituted vinyl radical intermediate is disfavored, probably due to the steric hindrance expected by the $SnMe_3$ moiety present in the molecule. Under these conditions, reduction is the preferred reaction pathway followed by the radical.

**TABLE 2. Palladium-Catalyzed Cross-Coupling Reactions of Vinylstannanes 2a and 5c with Iodoarenes in MeCN**[a]

| expt | vinylstannane (amt, mmol) | ArI (amt, mmol) | time, h | product, yield, %[b] |
|---|---|---|---|---|
| 1 | **2a** (0.10) | $p$-$MeOC_6H_4I$ (0.25) | 24 | **6a**,[c] 41 |
| 2 | **2a** (0.11) | $p$-$MeOC_6H_4I$ (0.29) | 21 | **6a**, 87 (69) |
| 3 | **2a** (0.10) | PhI (0.28) | 21 | **6b**, 98 (79) |
| 4 | **2a** (0.23) | $p$-$MeC_6H_4I$ (0.60) | 21 | **6c**, 90 (74) |
| 5 | **2a** (0.10) | $p$-$ClC_6H_4I$ (0.25) | 22 | **6d**, 93 (72) |
| 6 | **2a** (0.10) | 1-$C_{10}H_7$ (0.26) | 34 | **6e**, 89 (67) |
| 7 | **5c**(0.10) | $p$-$MeC_6H_4I$ (0.23) | 12 | **7a**,[c] 96 (78) |
| 8 | **5c**(0.15) | $p$-$ClC_6H_4I$ (0.31) | 13 | **7b**,[c] 94 (81) |

[a] Conditions: $Pd_2(dba)_3$ (9.0 mol %), P($o$-tolyl)$_3$ (20.0 mol %), CsF (2.5 equiv), MeCN (8 mL), 80 °C. [b] Determined by GLC using the internal standard method. The values in parentheses indicate the yields of the one-pot reactions. In one-pot experiments 1−6, ($E$)-stilbene was detected. [c] No CsF was added to the reaction.

Mitchell prepared 1,1-distannyl-1-alkenes from (trimethylstannyl)lithium and geminal dibromoalkenes in THF. However, when 1,1-dichloroalkenes **4a** and **4b** were employed in the same experimental conditions, hexamethylditin and the corresponding alkyne were obtained.[6]

All the above results indicate that the $S_{RN}1$ mechanism is a method that allows vinylstannanes to be obtained in very good yields through reactions of vinyl chlorides with $Me_3Sn^-$ in liquid ammonia.

**Cross-Coupling Reactions.** We began our study on the reaction of **2a** with PhI in different solvents and catalytic systems. No cross-coupling was achieved with the following systems: (i) catalyst, $Pd(PPh_3)_2Cl_2$; solvents, DMF, toluene; (ii) catalyst, $PdCl_2(PhCN)_2$; solvent, DMF; (iii) catalyst, $Pd_2(dba)_3$; $Ph_3As$ as ligand and CuI as additive; solvent, MeCN. With the catalytic system $Pd_2(dba)_3$ and P($o$-tolyl)$_3$ as ligand in MeCN as solvent, 1,1,2-triphenylethene was achieved in 79% yield after 22 h at 80 °C. Under the same experimental conditions, a 41% yield of the cross-coupling product was obtained with $p$-iodoanisole as electrophile (experiment 1, Table 2).

The limitations of the Stille reaction are probably due to steric hindrance in the transmetalation step. In other words, the steric effects of 1-substituted vinylstannanes cause them to be poorly reactive substrates.

Few examples of the Stille coupling with 1-substituted vinylstannanes employing $Pd_2(dba)_3$, P($o$-tolyl)$_3$, and CuI (MeCN, 80 °C, 15 h) are known to give unsatisfactory yields of cross-coupling products (27−42%).[25]

On the other hand, a protocol has been developed for coupling that implies the use of $Pd(PPh_3)_4$/CuCl/LiCl under anaerobic conditions in DMSO at 60 °C, showing excellent conditions for a variety of Stille couplings.[26]

Also it is known that tin is fluorophilic; Fu et al. employed CsF to enhance the reactivity of the organotin

---

[22] Galli, C.; Guarnieri, A.; Koch, H.; Mencarelli, P.; Rappoport, Z. *J. Org. Chem.* **1997**, *62*, 4072−4077.

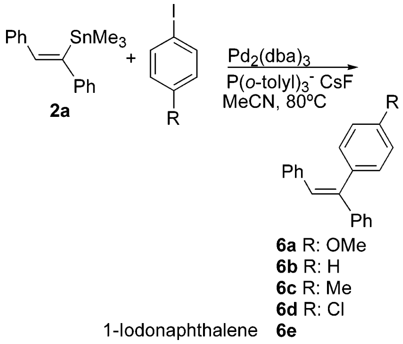
[23] Parkinson, C. J.; Pinhey, J. T.; Stoermer, M. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1911−1915.

[24] Bellina, F.; Carpita, A.; Fontana, E. A.; Rossi, R. *Tetrahedron* **1994**, *50*, 5189−5202.

[25] Liron, F.; Gervais, M.; Peyrat, J. F.; Alami, M.; Brion, J. D. *Tetrahedron Lett.* **2003**, *44*, 2789−2794.

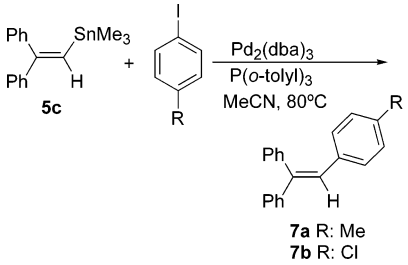
[26] Han, X.; Stoltz, B. M.; Corey, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 7600−7605.

compound in the Stille reaction with aryl chlorides.[27] We thought that CsF as additive would help the coupling of **2a** with iodoarenes, activating the transmetalation step. Thus, we carried out the reaction of **2a** with *p*-iodoanisole, but adding 2.6 equiv of CsF. After 21 h, the reaction affords an 87% yield of coupling product 1-methoxy-4-((*Z*)-1,2-diphenylvinyl)benzene (**6a**) (experiment 2, Table 2) (eq 3). Under these conditions the reaction with several iodoarenes (iodobenzene, *p*-iodotoluene, *p*-chloroiodobenzene, and 1-iodonaphthalene) gave in all cases the corresponding triarylolefin in 89−98% yield (experiments 3−6, Table 2) (eq 3).



(3)

The reaction of *p*-iodotoluene and *p*-chloroiodobenzene with the less hindered trimethyl(2,2-diphenylvinyl)stannane (**5c**) gave the cross-coupling products in shorter reaction time and in the absence of CsF (experiments 7 and 8, Table 2) (eq 4).



(4)

In all the cases studied, only the *ipso* cross-coupling products were formed. The palladium-catalyzed cross-coupling reaction of vinylstannanes with electrophilic halides affords a mixture of *ipso*- and *cine*-substituted products.[28] A number of reports indicate that, for a given vinylstannane, the *ipso*/*cine* ratio and the efficiency of the reaction are influenced by the position of electron-withdrawing groups on the electrophilic halides and the nature of the coupling conditions employed, among other factors.[26] However, it is not yet apparent how these factors influence the *ipso*/*cine* selectivity on the basis of the accepted mechanism for the formation of the *cine*-substituted products.[29]

We also explored the possibility of performing the synthesis of the vinylstannane and the Stille reaction in a one-pot-type reaction. Therefore, we carried out the $S_{RN}1$ reaction employing **1a** in liquid ammonia and $Me_3Sn^-$ ions to obtain the vinylstannane **2a**. The reaction was quenched by adding MeI.[30] Then the ammonia was allowed to evaporate and replaced by MeCN. To this solution were added the corresponding iodoarene and the catalyst system ($Pd_2(dba)_3$, $P(o\text{-tolyl})_3$, and CsF), and the resulting solution was heated at 80 °C for the time indicated in Table 2 (eq 5).

$$\mathbf{1a} \xrightarrow[\substack{\text{b) ArI, } Pd_2(dba)_3 \\ P(o\text{-tolyl})_3^- \text{ CsF} \\ \text{MeCN, 80ºC}}]{\text{a) } Me_3Sn^-,\ S_{RN}1} \mathbf{6a\text{-}e} \qquad (5)$$

The $S_{RN}1$ reaction to obtain vinylstannane **5c** is performed with **4c** and must be irradiated for 1 h. Then the methodology is similar. The yields of the coupling products are reported in Table 2.

In summary, the addition of CsF to the Stille couplings of 1,2-diarylvinylstannanes (1-substituted vinylstannanes) and haloarenes with $Pd_2(dba)_3$ as catalyst and the ligand $P(o\text{-tolyl})_3$ in MeCN enhances the reactivity of the system, giving very goods yields of triarylolefins. The vinylstannanes are obtained by efficient reactions of vinyl chlorides with $Me_3Sn^-$ in liquid ammonia by the $S_{RN}1$ mechanism.

## Experimental Section

**Materials.** *p*-Chloroiodobenzene, *p*-iodotoluene, *p*-iodoanisole, 1-iodonaphthalene, and iodobenzene were commercially available and used as received. (*Z*)- and (*E*)-1-chloro-1,2-diphenylethene (**1a** and **1b**) were obtained by chlorination (addition of hydrochloric acid to a solution of potassium permanganate in acetonitrile) of *trans*-stilbene,[31] giving the vicinal dichloroalkanes, and then treatment with ethanolic potassium hydroxide at reflux. The mixture was purified on a chromatographic column, employing petroleum ether as eluent: **1a**, colorless prism, mp 50−51 °C (lit.[32] mp 51−52 °C); **1b**, yellow liquid.[32] The vinylstannanes synthesized are all known compounds and were vacuum distilled using a Kügelrohr apparatus. 1,1-Dichloro-1-alkenes 2,2-dichlorovinylbenzene (**4a**), 1-(1,1-dichloroprop-1-en-2-yl)benzene (**4b**), and 1,1-dichloro-2,2-diphenylethene (**4c**) were prepared from the appropriate ketone or aldehyde, triphenylphosphine, and carbon tetrachloride (Wittig-type reaction).[33] **4a** and **4b** were purified by vacuum distillation using a Kügelrohr apparatus as viscous oils.[33,34] **4c** was purified by column chromatography, with petroleum ether as eluent, mp 78−79 °C (lit.[33] mp 78−78.5 °C).

**Photostimulated Reaction of $Me_3Sn^-$ Ions in Liquid Ammonia.** Irradiation was conducted in a reactor equipped with two 250 W UV lamps emitting maximally at 350 nm (water-refrigerated). The following procedure of the reaction of 1,1-dichloro-2,2-diphenylethene with $Me_3Sn^-$ ions is representative of all the reactions. Into a three-necked, 250 mL, round-bottomed flask equipped with a coldfinger condenser charged with dry ice−ethanol, a nitrogen inlet, and a magnetic

---

[27] Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2411−2413.

[28] (a) Levin, J. I. *Tetrahedron Lett.* **1993**, *34*, 6211−6214. (b) Chen, S. *Tetrahedron Lett.* **1997**, *38*, 4741−4744. (c) Quayle, P.; Wang, J.; Xu, J. *Tetrahedron Lett.* **1998**, *39*, 489−492. (d) Flohr, A. *Tetrahedron Lett.* **1998**, *39*, 5177−5180.

[29] (a) Busacca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Rodger, C. A. *J. Org. Chem.* **1994**, *59*, 7553−7556. (b) Farina, V.; Hossain, M. A. *Tetrahedron Lett.* **1996**, *37*, 6997−7000. (c) Fillion, E.; Taylor, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 12700−12701.

[30] The excess of $Me_3SnNa$ would react with methyl iodide to form $Me_4Sn$. It is more difficult to transfer a methyl group than a vinyl moiety.

[31] Liu, L. K.; Lin, C. S. *J. Chin. Chem. Soc.* **1996**, *43*, 61−66.

[32] Kropp, P. J.; Crawford, S. D. *J. Org. Chem.* **1994**, *59*, 3102−3112.

[33] Rabinowitz, R.; Marcus, R. *J. Am. Chem. Soc.* **1962**, *84*, 1312−1313.

[34] Braverman, S.; Zafrani, Y. *Tetrahedron* **1998**, *54*, 1901−1912.

stirrer was condensed 200 mL of ammonia previously dried with sodium metal under nitrogen. $Me_3SnCl$ (2.00 mmol) and sodium metal (4.80 mmol) were added; 0.50 mmol of vinyl chloride was added to this solution, and the resulting solution was then irradiated for 60 min. The reaction was quenched by adding $NH_4NO_3$ in excess, and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with diethyl ether. The chloride ions in the aqueous solution were determined potentiometrically. The product was quantified by GLC using the internal standard method. The spectroscopic data agreed with those reported in the literature.[20]

**Data for trimethyl((*Z*)-1,2-diphenylvinyl)stannane (2a):** white solid; mp 55−56 °C (lit.[20] mp 57 °C); $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 0.29 (s, 9 H, $^2J(^{119}SnCH) = 54.5$ Hz), 7.31−7.43 (m, 10 H), 7.52 (s, 1 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ −7.7 (353.4 Hz), 126.7, 127.4, 127.6 128.5, 129.0, 129.0, 138.7, 141.3, 143.2, 148.7 (415.0 Hz); MS [EI, *m/z* (rel intens)] 329 (64, $M^+ - CH_3$), 327 (62), 299 (9), 179 (100).

**Data for trimethyl((*E*)-1,2-diphenylvinyl)stannane (2b):**[20] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 0.27 (s, 9 H, $^2J(^{119}SnCH) = 53.1$ Hz), 6.75 (s, 1 H) 7.03−7.29 (m, 10 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ −9.8 (338.7 Hz), 126.9, 127.3, 127.7 128.9, 129.5, 131.2, 137.9, 142.8, 146.3, 149.1 (441.3 Hz); MS [EI, *m/z* (rel intens)] 329 (64, $M^+ - CH_3$), 327 (60), 299 (7), 178 (100).

**Data for trimethyl(2,2-diphenylvinyl)stannane (5c):**[20] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 0.32 (s, 9 H, $^2J(^{119}SnCH) = 52.8$ Hz), 6.74 (s, 1 H, $^2J(^{119}SnCH) = 68.0$ Hz) 7.25−7.39 (m, 10 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ −8.8 (340.1 Hz), 126.7, 127.1, 127.6, 128.0, 128.4, 129.6, 132.3 (447.0 Hz), 141.3, 142.6, 158.1. MS [EI, *m/z* (rel intens)] 329 (100, $M^+ - CH_3$), 327 (73), 313 (4), 297 (11), 179 (98).

**Data for (*E*)-trimethyl(styryl)stannane (5a):**[20] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 0.33 (s, 9 H, $^2J(^{119}SnCH) = 54.4$ Hz), 6.98 (s, 2 H, $^2J(^{119}SnCH) = 75.9$ Hz) 7.30−7.50 (m, 5 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ −9.7 (349.5 Hz), 126.5, 128.9, 127.7 129.7 (449.8 Hz), 138.3, 147.5; MS [EI, *m/z* (rel intens)] 253 (100, $M^+ - CH_3$), 239 (2), 223 (20), 104 (15), 77 (16).

**Data for (*Z*)-trimethyl(styryl)stannane (5a):**[20] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 0.33 (s, 9 H, $^2J(^{119}SnCH) = 54.8$ Hz), 6.33 (d, 1 H, $^2J(^{119}SnCH) = 64.3$ Hz, $J_{HH} = 13.1$ Hz) 7.32−7.48 (m, 5 H), 7.65 (d, 1 H, $J_{HH} = 12.7$ Hz); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ −9.0 (350.9 Hz), 126.8; 126.8, 128.7, 135.4 (430.7 Hz), 137.9, 149.5; MS [EI, *m/z* (rel intens)] 268 (1, $M^+$), (253 (100, $M^+ - CH_3$), 239 (2), 223 (14), 104 (18).

**Data for (*E*)-trimethyl(2-phenylpropen-1-yl)stannane (5b):**[23,24] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 0.21 (s, 9 H, $^2J(^{119}SnCH) = 54.7$ Hz), 2.27 (s, 3 H), 6.23 (s, 1 H, $^2J(^{119}SnCH) = 72.9$ Hz), 7.15−7.47 (m, 5 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ −8.9 (331.2 Hz), 27.4, 126.6, 128.4, 128.5, 142.3, 143.3, 155.4 (445.4 Hz); MS [EI, *m/z* (rel intens)] (267 (100, $M^+ - CH_3$), 266 (39), 265 (74), 263 (53), 237 (16), 115 (13).

**Data for (*Z*)-trimethyl-(2-phenylpropen-1-yl)stannane (5b):**[23,24] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ −0.16 (s, 9 H, $^2J(^{119}SnCH) = 53.8$ Hz), 2.23 (d, 3 H, $J = 1.6$ Hz), 5.87 (q, 1 H, $J = 1.4$ Hz), 7.05−7.43 (m, 5 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ −8.4 (340.3 Hz), 24.2, 127.5, 127.6, 130.7, 141.3, 141.9, 154.7 (429.6 Hz); MS [EI, *m/z* (rel intens)] (267 (100, $M^+ - CH_3$), 266 (37), 265 (71), 263 (48), 237 (15), 115 (14)

**Cross-Coupling Reaction of 2a with PhI Catalyzed by $Pd_2(dba)_3$, P(*o*-tolyl)$_3$, and CsF in MeCN.** The following procedure is representative of all the reactions. Into a three-necked, 50 mL, round-bottomed flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer was added 8 mL of MeCN, and afterward, the stannane **2a** (0.10 mmol), the iodoarene in excess, for instance, iodobenzene (0.28 mmol), the catalyst system $Pd_2(dba)_3$ (9.0 mol %), P(*o*-tolyl)$_3$ (20.0 mol %), and CsF (0.70 mmol), and the solution were heated to 80 °C for 21 h. The solution was filtered, water (30 mL) was added to the residue, and then the residue was extracted three times with diethyl ether. The product was quantified by GLC using the internal standard method compared with authentic samples. Product **6b** was isolated by column chromatography on silica gel (eluent petroleum ether): mp 69−70 °C (lit.[2] mp 67−69 °C); MS [EI, *m/z* (rel intens)] 256 (100, $M^+$), 178 (57).

**Sequential Reactions of $Me_3Sn^-$ Ions with 1a Followed by Palladium-Catalyzed Cross-Coupling Reaction with Iodoarenes.** The following procedure is representative of all the reactions. Into a three-necked, 250 mL, round-bottomed flask was condensed 200 mL of dry liquid ammonia. $Me_3SnCl$ (2.3 mmol) and sodium metal (5.0 mmol) were added. To this solution was added 0.50 mmol of **1a**. After 10 min the reaction was quenched by adding MeI in excess, the ammonia was allowed to evaporate, and the residue was dissolved in MeCN (8 mL). To this solution were added the corresponding iodoarene (1.25 mmol) and the catalyst system $Pd_2(dba)_3$ (8.8 mol %), P(*o*-tolyl)$_3$ (20 mol %), and CsF (2.5 equiv, 3.15 mmol), and the resulting solution was heated at 80 °C for the time indicated in Table 2. Then the procedure was similar to that of the previous reactions. To obtain vinylstannane **5c**, the solution of **4c** and $Me_3Sn^-$ ions was irradiated for 1 h.

**Data for (*Z*)-1-(4-methoxyphenyl)-1,2-diphenylethylene (6a):** purified by column chromatography on silica gel employing petroleum ether as eluent; mp 89−90 °C (lit.[35] mp 90−91 °C); $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 3.81 (s, 3 H), 6.82 (d 2 H, $J = 8.3$ Hz), 6.93 (s, 1 H), 7.01−7.15 (m, 5 H), 7.19−7.26 (m, 7 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ 52.3, 114.5, 126.2, 126.9, 127.3, 127.7, 128.4, 129.0, 129.8, 130.7, 136.2, 137.4, 141.7, 143.3, 157.6; MS [EI, *m/z* (rel intens)] 286 (100, $M^+$), 270 (8), 253 (15), 178 (18).

**Data for (*Z*)-1-(4-methylphenyl)-1,2-diphenylethylene (6c):** purified by column chromatography on silica gel (eluent petroleum ether); colorless liquid;[36] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 2.29 (s, 3 H), 6.91−7.24 (m, 15 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ 20.7, 113.3, 127.6, 127.9, 128.3, 128.7, 129.0, 129.3, 129.9, 130.7, 136.5, 137.4, 140.6, 141.0, 142.9; MS [EI, *m/z* (rel intens)] 270 (100, $M^+$), 255 (40), 193 (12), 178 (37).

**Data for (*Z*)-1-(4-chlorophenyl)-1,2-diphenylethylene (6d):** purified by column chromatography on silica gel (eluent petroleum ether); mp 91−93 °C (lit.[37] mp 92−93 °C); $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 6.87 (s, 1 H), 7.05−7.25 (m, 14 H); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ 127.7, 128.3, 128.9, 129.2, 131.1, 131.5, 132.6, 132.9, 133.8, 134.7, 137.5, 140.6, 141.1, 142.9; MS [EI, *m/z* (rel intens)] 290 (100, $M^+$), 255 (32), 178 (24).

**Data for (*Z*)-1-(1-naphthyl)-1,2-diphenylethylene (6e):** purified by column chromatography on silica gel (eluent petroleum ether) and vacuum distillation using a Kügelrohr apparatus as an oil;[38] $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 6.92−7.10 (m, 2H), 7.22−7.37 (m, 3 H), 7.45−7.60 (m, 10 H), 7.83 (d, 1 H, $J = 8.0$ Hz), 7.93 (d, 1 H, $J = 8.2$ Hz), 7.98 (d, 1 H, $J = 7.9$ Hz); $^{13}$C NMR (50.288 MHz, $CDCl_3$) $\delta$ 124.1, 124.3, 124.8, 125.5, 126.2, 126.7, 127.6, 128.5, 128.9, 129.3, 129.7, 130.2, 131.7, 132.9, 135.2, 136.9, 137.1, 138.7, 141.9; MS [EI, *m/z* (rel intens)] 306 (68, $M^+$), 228 (100), 178 (24).

**Data for 1,1-diphenyl-2-(4-methylphenyl)ethene (7a):** purified by column chromatography on silica gel employing petroleum ether as eluent; mp 73−74 °C (lit.[39] mp 74 °C); $^1$H NMR (200.13 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 2.31 (s, 3 H), 6.93 (s, 1

---

(35) Curtin, D. Y.; Harris, E. E.; Meislich, E. K. *J. Am. Chem. Soc.* **1952**, *74*, 2901−2904.

(36) Effenberger, F.; Russ, W. *Chem. Ber.* **1982**, *115*, 3719−3736.

(37) Curtin, D. Y.; Harris, E. E. *J. Am. Chem. Soc.* **1951**, *73*, 2716−2717.

(38) M. Alami et al. obtained this compound by palladium-catalyzed cross-coupling reaction of 1-(2-iodo-2-phenylvinyl)naphthalene and phenylzinc chloride in 79% yield. The spectroscopic data agreed with those reported in the literature, ref 25.

(39) Bergmann, F.; Dimant, E.; Japhe, H. *J. Am. Chem. Soc.* **1948**, *70*, 1618−1620.

H), 7.13−7.24 (m, 14 H); $^{13}$C NMR (50.288 MHz, CDCl$_3$) $\delta$ 21.3, 128.0, 128.9, 131.3, 132.1, 134.8, 135.5, 141.9, 142.4, 142.7, 143.1; MS [EI, *m*/*z* (rel intens)] 270 (100, M$^+$), 254 (21), 178 (30).

**Data for 1,1-diphenyl-2-(4-chlorophenyl)ethene (7b):** purified by column chromatography on silica gel employing petroleum ether as eluent; mp 76−77 °C (lit.[40] mp 76−76.5 °C); $^1$H NMR (200.13 MHz, CDCl$_3$, Me$_4$Si) $\delta$ 6.89 (s, 1 H), 7.09−7.23 (m, 14 H); $^{13}$C NMR (50.288 MHz, CDCl$_3$) $\delta$ 128.5, 128.8, 130.6, 131.0, 131.3, 134.2, 135.6, 140.8, 141.3, 142.8; MS (EI, *m*/*z* (rel intens)] 290 (100, M$^+$), 255 (15), 178 (11).

**Acknowledgment.** This work was supported in part by the Consejo de Investigaciones de la Provincia de Córdoba (CONICOR), the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), SECYT, the Universidad Nacional de Córdoba, the Antorchas Foundation, and FONCYT, Argentina. E.F.C. gratefully acknowledges receipt of a fellowship from CONICET.

JO049287Z

---

(40) Pedersen, C. Th. *Acta Chem. Scand.* **1968**, *22*, 247−253.