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Palladium-Catalyzed Markovnikov Terminal Arylalkynes Hydrostannation: Application to the Synthesis of 1,1-Diarylethylenes

Abdallah Hamze, Damien Veau, Olivier Provot, Jean-Daniel Brion, and Mouâd Alami*

Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie, Universite Paris-Sud, CNRS, BioCIS, UMR 8076, rue J. B. Clément, Châtenay-Malabry, F-92296, France

mouad.alami@u-psud.fr

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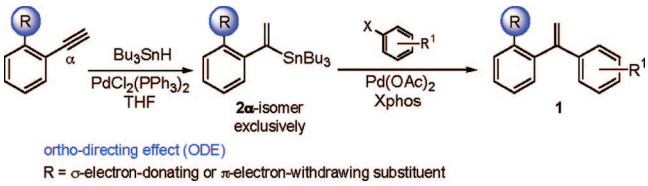
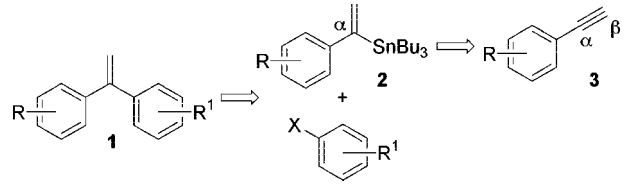


The palladium-catalyzed hydrostannation of terminal arylalkynes was achieved. The regioselectivity of the H−Sn bond addition across the triple bond was found to be controlled by an ortho substituent on the aromatic ring, whatever its electronic nature, to give exclusively α-branched vinylstannanes **2** in accordance with Markovnikov's rule. Subsequent Stille cross-coupling reaction of **2** with a variety of aryl halides readily provided, in moderate to good yields, a family of functionalized 1,1-diarylethylenes **1**.

1,1-Diarylethylenes **1**, an important structural motif found in biologically active compounds,[1] can, in principle, be accessed[2] from terminal arylalkynes **3** via Stille cross-coupling reaction between intermediates **2** and aryl halides (Scheme 1).[3] In this strategy, two synthetic challenges remain to be solved. On the one hand, the *cine* substitution[4] constitutes a major limitation which is most frequently encountered in the Stille coupling of sterically encumbered 1-substituted vinylstannanes of type **2**. Additionally, there are no available procedures for effecting this coupling in good yield. On the other hand, the literature methods for the synthesis of α-styryltributyltin[5] **2** from **3** afforded a mixture of regioisomeric vinylstannanes which resist chromatographic separation.[6] Consequently, the regiochemical control of the hydrostannation of terminal arylalkynes **3** has remained a prominent unanswered synthetic challenge. In the present work, these problems have been overcome.

SCHEME 1



Previously, we reported the effect of ortho substituents on the regioselectivity in the transition-metal (Pd, Pt)-catalyzed hydrostannation[7] and hydrosilylation[8] of aryl-substituted alkynes and related compounds.[9] In the case of internal arylalkynes, such as diarylalkynes and aliphatic arylalkynes, we demonstrated that the presence of an ortho substituent on arylalkynes promoted a highly regioselective addition of the metal hydride to the triple bond, regardless of the electronic nature of the substituent (π-electron-withdrawing or σ-electron-donating group). Thus, the hydrometalation formed a single product where the metal moiety ($SnBu_3$, SiR_3) was delivered to the carbon proximal to the ortho-substituted aryl nucleus. Encouraged by these results, we envisioned to extend this ortho-directing effect (ODE) to terminal arylalkynes **3** in order to provide α-branched vinylmetal species of type **2**, suitable for the synthesis of 1,1-diarylethenes **1**. In the case of the Pt-catalyzed hydrosilylation of terminal

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(4) When styrylstannanes are coupled with aryl halides, a reversal of regioselectivity is often observed with formation of (*Z*)- and (*E*)-*cine* substitution regioisomers. (a) Stork, G.; Isaacs, R. C. A. *J. Am. Chem. Soc.* **1990**, *112*, 7399–7400. (b) Levin, J. I. *Tetrahedron Lett.* **1993**, *34*, 6211–6214. (c) Quayle, P.; Wang, J.; Xu, J.; Urch, C. J. *Tetrahedron Lett.* **1998**, *39*, 489–492. (d) Flohr, A. *Tetrahedron Lett.* **1998**, *39*, 5177–5180. (e) Fillion, E.; Taylor, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 12700–12701, and references therein.

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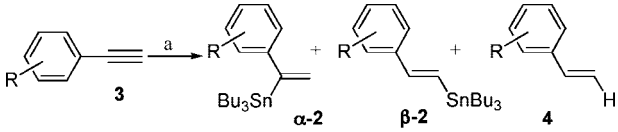
TABLE 1. Hydrostannation of Para- and Meta-Substituted Terminal Arylalkynes: Effect of Substitution Pattern on Regioselectivity[a]



a : $PdCl_2(PPh_3)_2$ 2 mol%, Bu_3SnH 1.2 equiv, THF, rt

Entry	Alkyne **3**	Ratio[b] (**α-2:β-2:4**)	Yield[c] (%)
1	**3a**	49:51:0	88[d]
2	**3b** (OMe)	35:0:65	nd[e]
3	**3c** (OMe)	71:0:29	nd[e]
4	**3d** (Me)	50:0:50	nd[e]
5	**3e** (CH_2OH)	66:0:34	58[f]
6	**3f** (OBn)	61:39:0	77[d]
7	**3g** (Br)	78:0:22	74[f]
8	**3h** (CO_2Me)	85:15:0	86[d]
9	**3i** (CN)	93:7:0	78[d]
10	**3j** (CHO)	95:0:5	83[f]

[a] All reactions were conducted with Bu_3SnH (1.2 equiv) in the presence of 2 mol % of $PdCl_2(PPh_3)_2$ in THF. [b] Ratio was determined by ^1H of the crude reaction mixture. [c] Isolated yield. [d] The product was isolated as a mixture of **α-2/β-2** regioisomers. [e] Not determined. [f] The product was isolated with inseparable side product **4**.

TABLE 2. Hydrostannation of Ortho-Substituted Terminal Arylalkynes 3 To Give Markovnikov Addition Products α-2[a]

Entry	Alkyne **3**	Ratio[b] (**α-2:β-2:4**)	Vinyl-stannane **α-2**	Yield[c] (%)
1	MeO **3k**	100:0:0	SnBu3, OMe **α-2k**	65
2	Me **3l**	100:0:0	SnBu3, Me **α-2l**	76
3	HOH_2C **3m**	100:0:0	SnBu3, CH_2OH **α-2m**	64
4	BnO **3n**	100:0:0	SnBu3, OBn **α-2n**	65
5	Br **3o**	100:0:0	SnBu3, Br **α-2o**	93
6	MeO_2C **3p**	100:0:0	SnBu3, CO_2Me **α-2p**	87
7	NC **3q**	100:0:0	SnBu3, CN **α-2q**	73
8	OHC **3r**	100:0:0	SnBu3, CHO **α-2r**	75

[a] All reactions were conducted with Bu_3SnH (1.2 equiv) in the presence of 2 mol % of $PdCl_2(PPh_3)_2$ in THF. [b] Ratio was determined by ^1H of the crude reaction mixture. [c] Yield refers to isolated pure **α-2** products.

alkynes, although conditions producing exclusively the β-isomer have been developed by our group,[10] we did not succeed in synthesizing selectively the α-isomer,[11] even with alkyne substrates bearing an ortho-directing substituent.[8b] For the success of our goal, we decided to examine the ability of ODE to produce regioselectively α-styryltributyltin derivatives **2**. The results of this study are now discussed.

In our initial screening conditions, phenylacetylene was evaluated as baseline control. An almost equal product distribution (**α-2a/β-2a** = 49/51) was obtained for the hydrostannation of phenylacetylene with Bu_3SnH in the presence of $PdCl_2(PPh_3)_2$ (2 mol %) in THF (Table 1, entry 1). The effect of substitution patterns on regioselectivity was then evaluated. With para- or meta-substituted phenylacetylenes bearing an electron-donating group, except for benzyloxy group, no β-isomer could be observed, but the reaction gave a mixture of inseparable α-isomers **2** and olefins **4** (entries 2−5). Surprisingly, with 4-benzyloxyphenylacetylene **3f**, no trace of the corresponding olefin **4f** was detected, but the hydrostannation proceeded with a modest regioselectivity (**α-2f/β-2f** = 61/39, entry 6). As expected, this trend in α-selectivity is more marked with para-substituted phenylacetylenes bearing π-electron-withdrawing groups which induced strong polarization of the carbon−carbon triple bond. Thus, a strong preference for α-branched vinylstannane products (**α-2** = 78 to 95) is observed with para-substituted phenylacetylene bearing a bromo, a methoxycarbonyl, a cyano, or a formyl substituent (entries 7−10).

As summarized in Table 2, under identical reaction conditions, all ortho substituents, regardless of their electronic nature, directed the tin moiety to the sterically more hindered α-position of the triple bond to give exclusively branched styrylstannanes **α-2** in good to excellent yields (entries 1−8). In these cases, no side products of type **4** were detected. Noteworthy is the tolerance of the reaction for a variety of functional groups, including bromides, free alcohols, esters, nitriles, and aldehydes. These results clearly demonstrated that the ortho substituent regiocontrol concept could be also successfully extended to the palladium-catalyzed hydrostannation of terminal arylalkynes to provide a general access to α-styryltributyltin derivatives **2**. With the series of α-styrylstannanes in hand, we then focused our attention on their coupling with a variety of aryl halides. Although Stille coupling has already been established as an efficient method for the formation of carbon−carbon bonds, the reaction with sterically hindered α-branched vinylstannanes is

(10) For the regioselective formation of β-(*E*)-vinylsilanes from terminal arylalkynes, see: (a) Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *Tetrahedron Lett.* **2008**, *49*, 2429–2431. (b) Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *J. Organomet. Chem.* **2008**, *693*, 2789–2797.

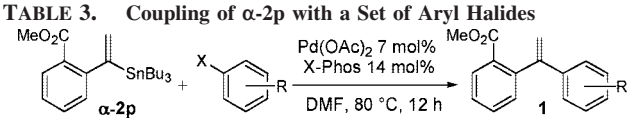
(11) For the Ru-catalyzed Markovnikov terminal alkyne hydrosilylation, see: Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726–12727.

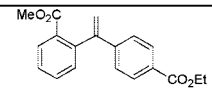
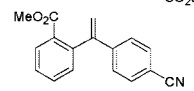
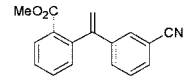
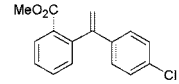
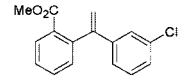
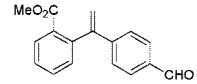
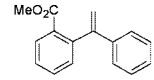
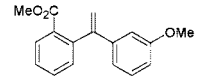
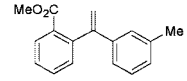
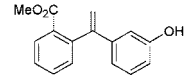
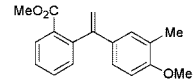
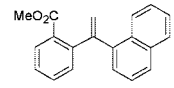
far from trivial due to very slow reaction rates[12] and competing *cine* substitution. To find the proper reaction conditions, the coupling of ortho-substituted styryltributyltin **α-2p** with ethyl 4-iodobenzoate was selected as a model reaction. Reaction conditions, such as Pd source, ligand, solvent, and additive,[13] were examined based on several reported Stille conditions. After an extensive study, optimal conditions were found to require **α-2p** (1.0 equiv), ethyl 4-iodobenzoate (1.2 equiv), $Pd(OAc)_2$ (7 mol %), and XPhos (14 mol %) in DMF at 80 °C. Thus, 1,1-diarylethylene **1a** was formed in a 72% satisfactory yield (Table 3, entry 1). It should be noted that a careful examination of the crude reaction mixture by ^1H revealed the absence of the *cine* substitution product.

Further investigations of the efficiency and scope of the present method were performed with styryltributyltin **α-2p** having an electron-withdrawing substituent. As seen in Table 3, the protocol described above proved to be quite general, allowing the coupling to proceed with a variety of aryl halide groups substituted, including iodides and bromides. Both electron-withdrawing (entries 1−6) and electron-donating (entries 8−12) aryl halides were coupled cleanly to provide the corresponding 1,1-diarylethylenes **1** in moderate to good yields. As expected, electron-poor aryl iodides delivered 1,1-diarylethylenes **1** in higher yields (entries 1−5) than those bearing an electron-donating substituent (entries 8−11). Even switching the substituent from the para to the meta position of the aryl moiety did not affect significantly the coupling yield (entries 2 and 4 vs entries 3 and 5). It may be pointed out that Stille coupling of **α-2p** with a lower reactive aryl bromide provided the expected 1,1 diarylethylene **1f** in a good yield (entry 6). Finally, it is apparent that the coupling tolerated a number of functional groups, including esters (entry 1), nitriles (entries 2 and 3), sp^2 chlorides (entries 4 and 5), aldehydes (entry 6), and free alcohols (entry 10).

With the feasibility of the Stille reaction of electron-poor styrylstannane **α-2p** secured, we then focused on the coupling of an electron-rich α-styrylstannane with various aryl halides. To this end, **α-2k** with an ortho methoxy substituent on the aryl nucleus and ethyl 4-iodobenzoate were mixed under the previous optimal conditions. However, the reaction failed and the vinylstannane **α-2k** was recovered unchanged together with notable amounts of the ethyl 4-iodobenzoate homocoupling product. Addition of CuI or CsF at higher temperatures gave low yields of the coupling product **1m** (<15%), whereas a combination[14] of the two salts gave an improved 51% yield. After extensive optimization, we found that Stille coupling of **α-2k** (1 equiv) with ethyl 4-iodobenzoate (0.9 equiv) using $Pd(OAc)_2$ (10 mol %), XPhos (20 mol %), CuI (20 mol %), and CsF (2 equiv) in DMF at 100 °C gave the expected 1,1-diarylethylene **1m** (Table 4, entry 1) in an acceptable 59% yield when the reaction was achieved in a sealed tube. Several aryl halides with different substitution patterns were tested and all coupled with satisfactory yields. The results are summarized in Table 4.

TABLE 3. Coupling of α-2p with a Set of Aryl Halides



Entry	X	R	1,1-Diarylethylene **1**		Yield[a] (%)
1	I	*p*-CO_2Et		**1a**	72
2	I	*p*-CN		**1b**	79
3	I	*m*-CN		**1c**	60
4	I	*p*-Cl		**1d**	63
5	I	*m*-Cl		**1e**	68
6	Br	*p*-CHO		**1f**	68
7	I	H		**1g**	57
8	I	*m*-OMe		**1h**	51
9	I	*m*-Me		**1i**	53
10	I	*m*-OH		**1j**	63
11	I	*p*-OMe *m*-Me		**1k**	54
12	I	1-naphtyl		**1l**	74

[a] Isolated yield of **1** after column chromatography. All the reported compounds exhibited spectral data in agreement with assigned structures.

As the Stille coupling of **α-2** with electron-poor aryl halides, the presence of an ortho electron-donating group on the styrylstannane **α-2k** did not affect significantly the reaction outcome (entries 1−3). 4-Bromobenzaldehyde reacted also under these conditions but gave **1p** with a modest 40% yield (entry 4). Finally, nonactivated aryl iodides such as iodobenzene and 3-iodotoluene reacted cleanly with **α-2k**, and there was a noticeable improvement in yields (entries 5 and 6).

To obviate direct manipulation and purification of the styryltributyltin coupling partner, we next examined a one-pot Pd-catalyzed hydrostannation/Stille coupling sequence as it would be economically and environmentally advantageous over multistep syntheses (Scheme 2). In a typical experiment, we achieved this transformation in a sequential way by mixing, in a first step, Bu_3SnH with terminal alkyne **3p** in THF under

(12) During the synthesis of orally active cephalosporins, Kawabata showed that, when performing the Stille coupling with a mixture of vinylstannanes **2a** and **2b**, only **2b** reacted, leading to a linear olefin as the sole product. Yamamoto, H.; Terasawa, T.; Ohki, A.; Shirai, F.; Kawabata, K.; Sakane, K.; Matsumoto, S.; Matsumoto, Y.; Tawara, S. *Bioorg. Med. Chem.* **2000**, *8*, 43–54.

(13) (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585–9595. (b) Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905–5911. (c) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033–3040. (d) Casado, A. L.; Espinet, P.; Gallego, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11771–11782.

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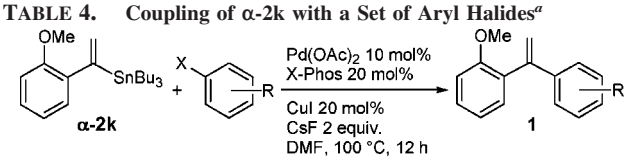
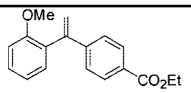
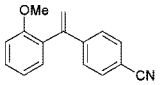
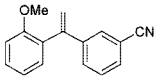
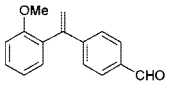
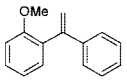
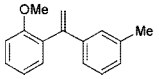
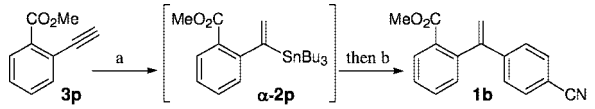
TABLE 4. Coupling of α-2k with a Set of Aryl Halides[a]



Entry	X	R	1,1-Diarylethylene **1**	Yield[b] (%)
1	I	*p*-CO_2Et	 **1m**	59[c]
2	I	*p*-CN	 **1n**	64
3	I	*m*-CN	 **1o**	63
4	Br	*p*-CHO	 **1p**	40[d]
5	I	H	 **1q**	67
6	I	*m*-Me	 **1r**	76

[a] Reactions were run in sealed tubes. [b] Isolated yield of **1** after column chromatography. All the reported compounds exhibited spectral data in agreement with assigned structures. [c] When exposing to microwave irradiation, the homocoupling of ethyl 4-iodobenzoate predominated and **1m** was isolated with a lower yield (28%). [d] The reaction conditions were not optimized.

SCHEME 2. One-Pot Synthesis of 1,1-Diarylethylene 1b from 3p via a Hydrostannation/Stille Reaction Sequence



a : $PdCl_2(PPh_3)_2$ (2 mol%) , Bu_3SnH (1.2 equiv) , THF, rt, 1 h
b : $Pd(OAc)_2$ (7 mol%) , XPhos (14 mol%), 4-iodobenzonitrile (1.2 equiv), DMF, 80 °C, 12 h

palladium catalysis. After removal of the solvent under reduced pressure, DMF, $Pd(OAc)_2$ (7 mol %), XPhos (14 mol %), and 4-iodobenzonitrile (1.2 equiv) were introduced in a second step and heated at 80 °C for 12 h. Thus, under this protocol, we were pleased to observe that the sequential reaction worked very well and provided the desired 1,1-diarylethylene **1b** in a 51% yield, despite the fact that the reaction conditions had never been optimized.

In summary, we have studied the palladium-catalyzed hydrostannation of terminal arylalkynes and demonstrated that the ortho substituent in alkyne substrates promotes the regioselective addition of Bu_3SnH to the triple bond. Thus, regardless of the electronic nature of the ortho substituent, this procedure provides a general route to α-styrylstannanes **2**. Additionally, we have succeeded in developing reaction conditions for the Stille coupling of various aryl halides with α-styrylstannanes **2** bearing either an electron-donating or an electron-withdrawing substituent at the ortho position of the aromatic ring. These new protocols have proved to be highly effective to avoid the problematic *cine* substitution, which is a well-documented side reaction in the palladium-assisted elaboration of α-styrylstannanes to 1,1-diarylethylenes **1**. More interestingly, a one-pot approach of this method that tolerates several functional groups is successfully enlightened, with the additional benefit of requiring only a single purification step. Additional investigations of the synthetic utility of this transformation into the synthesis of molecules of biological interest are currently underway and will be reported in due course.

Experimental Section

Representative Procedure for the Synthesis of 1a. To a mixture of $Pd(OAc)_2$ (15.72 mg, 0.07 mmol), Xphos (66.75 mg, 0.14 mmol), and **α-2p** (0.45 g, 1 mmol) in DMF (10 mL) was added dropwise ethyl 4-iodobenzoate (0,33 g, 1.2 mmol) in DMF (3 mL). The mixture was stirred under an argon atmosphere for 12 h at 80 °C, then cooled and diluted with an equal volume of saturated aqueous KF (13 mL). The two-phase mixture was stirred vigorously overnight then diluted with diethyl ether (20 mL). The separated organic layer was washed with saturated ammonium chloride (2 × 20 mL) and brine (20 mL), then dried and evaporated. Purification by chromatography on silica gel (cyclohexane/Et_2O 90/10) gave **1a** (223 mg, 72%): R_f 0.24 (cyclohexane/Et_2O 90/10); ^1H NMR (300 MHz) δ 7.87 (d, 2H, $J = 8.2$ Hz), 7.78 (dd, 1H, $J = 7.6$, 1.3 Hz), 7.48 (td, 1H, $J = 7.6$, 1.3 Hz), 7.40−7.16 (m, 2H), 7.20 (d, 2H, $J = 8.2$ Hz), 5.69 (s, 1H), 5.27 (s, 1H), 4.28 (q, 2H, $J = 7.1$ Hz), 3.43 (s, 3H), 1.30 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (75 MHz) δ 167.8 (C), 166.5 (C), 149.2 (C), 145.4 (C), 142.0 (C), 132.0 (CH), 131.5 (CH), 130.7 (C), 130.3 (CH), 129.6 (2CH), 129.5 (CH), 128.1 (CH), 126.5 (2CH), 116.1 (CH_2), 61.0 (CH_2), 51.9 (CH_3), 14.4 (CH_3); IR (ν, cm^{-1}) 2983, 1711, 1607, 1447, 1433, 1406, 1367, 1269, 1181, 1124, 1104, 1068, 1018, 964, 908, 863, 817, 772, 714; MS (ESI+) 311.1 $(M + H)^+$, 332.9 $(M + Na)^+$. Anal. Calcd for $C_{19}H_{18}O_4$ (310.34): C, 73.53; H, 5.85. Found: C, 73.41; H, 5.79.

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Supporting Information Available: Full experimental procedures, characterization data, copies of ^1H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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