Notes

Reactions of Vinyl and Aryl Triflates with Hypervalent Tin Reagents

Antonio García Martínez,* José Osío Barcina,*
María del Rosario Colorado Heras, and Álvaro de Fresno Cerezo

Departamento de Química Orgánica, Facultad de Ciencias Químicas,
Universidad Complutense, Ciudad Universitaria, 28040 Madrid, Spain

Received November 13, 2000

Summary: The reaction of hypervalent tin reagents $(n\text{-}Bu_4N)^+(R^1{}_3SnF_2)^-$ *(*R^1 *= aryl, benzyl) with vinyl and aryl triflates affords the corresponding cross-coupling products in good yields and short reaction times. The method described represents an important improvement over the classical Stille reaction. The hypervalent reagents are easily prepared by reaction of* $R^1{}_3SnF$ *and* $n\text{-}Bu_4NF$.

Introduction

The palladium-catalyzed cross-coupling reaction between organotin compounds and organic halides or triflates (the Stille reaction) is a widely used methodology for the formation of C−C bonds.[1,2] Although the Stille reaction has been applied successfully in a large number of cases,[1a] some coupling reactions fail or lead to poor yields. Thus, when vinyl triflates are used as the electrophile, only traces of the coupling products are obtained with Me_3SnPh or Me_3SnBn and $Pd(TPP)_4$ in THF.[3,4] On the other hand, the reaction of arylstannanes with aryl triflates works well if extreme reaction conditions are used,[5] and poor yields (21%) are obtained in the benzylation of aryl triflates.[6] Other possible organometallic derivatives for benzylation reactions are of limited applicability since the preparation of lithium dibenzylcopper (and related Gilman reagents)[7] and benzylic zinc reagents[6,8] is not easy due to the tendency of these reagents to give homocoupling byproducts. Suzuki cross-coupling reaction[9] has not been employed for benzylation reaction mainly due to the difficult accessibility of the corresponding benzylic boronates.[10,11]

Although some of the limitations of the Stille cross-coupling of triflates mentioned above (e.g., arylation of aryl triflates) can be overcome by changing the catalyst[1,5] or the solvent,[1a] the development of new modifications of this reaction is of great utility. In this paper we show that the Pd(0)-catalyzed reaction of vinyl and aryl triflates with hypervalent tin reagents is an important improvement over the classical Stille methodology.

Results and Discussions

We have recently reported the first examples of reactions of hypervalent tin reagents with vinyl and aryl triflates. The reactions of vinyl triflates with tetrabutylammonium difluorotriphenylstannate $[(n\text{-}Bu_4N)^+(Ph_3SnF_2)^-]$ (**1**)[12] and aryl triflates with tetrabutylammonium difluorotribenzylstannate $[(n\text{-}Bu_4N)^+(Bn_3SnF_2)^-]$ (**2**)[13] yield the corresponding cross-coupling products in good to high yields under mild reaction conditions (Scheme 1) (Table 1).[14] The effect of fluoride in these hypervalent tin complexes is to facilitate the transfer of the aryl or benzyl group in the transmetalation step of the reaction.

Hypervalent tin reagents **1** and **2** are easily prepared following the procedure described for **1** (Scheme 1).[15a] The reaction takes place in quantitative yield under mild conditions due to the high tendency of fluoride

---

* Corresponding author. Tel: 91 3944333. E-mail: josio@eucmos.sim.ucm.es.

(1) (a) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Organic Reactions*; Wiley: New York, 1997; Vol. 50. (b) Ritter, K. *Synthesis* **1993**, 735. (c) Mitchell, T. N. *Synthesis* **1992**, 803.

(2) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(3) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.

(4) A good yield (70%) in the benzylation of the vinyl triflate derived from 3-chromanone using $BnSnBu_3/(TPP)_2PdCl_2$/HMPA has been reported recently: (a) Usse, S.; Guillaumet, G.; Viaud, M.-C. *Tetrahedron Lett.* **1997**, *38*, 5501. For reactions of benzyl stannanes with acid chlorides, see: (b) Andrianome, M.; Delmond, B. *J. Org. Chem.* **1988**, *53*, 542. (c) Labadie, J. W.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4634.

(5) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434.

(6) de Lang, R.-J.; van Hooijdonk, M. J. C. M.; Brandsma, L.; Kramer, H.; Seinen, W. *Tetrahedron* **1998**, *54*, 2953.

(7) (a) Posner, G. H. *Org. React.* **1975**, *22*, 253. (b) Lipshutz, B. H. *Synlett* **1990**, 119.

(8) (a) Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117. (b) Rottländer, M.; Knochel, P. *Tetrahedron Lett.* **1997**, *38*, 1749.

(9) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(10) A procedure for the preparation of benzylic and allylic boronates has been recently reported: Falck, J. R.; Bondlela, M.; Ye, J.; Cho, S.-D. *Tetrahedron Lett.* **1999**, *40*, 5647.

(11) Reactions based on the coupling of benzylic electrophiles instead of benzylic stannanes or boronates have been described. For reactions of benzylic bromides and aryl stannanes, see: (a) Kamlage, S.; Sefkow, M.; Peter, M. G. *J. Org. Chem.* **1999**, *64*, 2938. Reactions involving benzylic bromides and aryl stannanes are described in: (b) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992. Cross-coupling between phenyl- or naphthylboronic acids and benzylic bromides have also been reported: (c) Chowdhury, S.; Georghiou, P. E. *Tetrahedron Lett.* **1999**, *75*, 7599. (d) Klärner, C.; Greiner, A. *Macromol. Rapid Commun.* **1998**, *19*, 605.

(12) García Martínez, A.; Osío Barcina, J.; de Fresno Cerezo, A.; Subramanian, L. R. *Synlett* **1994**, 1047.

(13) García Martínez, A.; Osío Barcina, J.; Colorado Heras, M. R.; de Fresno Cerezo, A. *Org. Lett.* **2000**, *2*, 1377.

10.1021/om000957a CCC: $20.00

Publication on Web 02/08/2001

Table 1. Reaction of Vinyl and Aryl Triflates with $(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$ (1) and $(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$ (2)

entry	triflate	stannate	reaction conditions	product (yield,%)	ref[a]
1	**3a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/30 min	**3b** (81)	12
2	**4a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/30 min	**4b** (83)	12
3		n-Bu$_4$NF/Ph$_3$SnF (2 eq.)	Pd(TPP)$_4$/THF/Δ/2 h	**4b** (40)	tw
4		n-Bu$_4$NF/Ph$_3$SnCl (2 eq.)	Pd(TPP)$_4$/THF/Δ/24 h	**4b** (17)	tw
5		n-Bu$_4$NF/Ph$_4$Sn	Pd(TPP)$_4$/THF/Δ/30 min	**4b** (68)	tw
6		n-Bu$_4$NF/Ph$_4$Sn (2 equiv)	Pd(TPP)$_4$/THF/Δ/1 h	**4b** (85)	tw
7		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/40 °C/30 min	**4c** (75)	tw
8	**5a**	$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/80 °C/15 min	**5c** (50)[b]	tw
9	**6a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/30 min	**6b** (84)	12
10		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/80 °C/4 min	**6c** (73)	tw
11	**7a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/30 min	**7b** (85)	12
12		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/80 °C/4 min	**7c** (40)	tw
13	**8a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/30 min	**8b** (85)	12
14	(*Z*/*E*)-**9a**[c]	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/30 min	(*Z*/*E*)-**9b** (83)[c]	12
15		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/100 °C/2 min	(*E*)-**9c** (52)[d]	tw
16	**10a**	$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/100 °C/4 min	**10c** (40)	tw
17	**11a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/12 h	**11b** (56)	tw
18		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/1 min	**11c** (68)[b]	13
19	**12a**	$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/1.5 h	**12c** (52)[b]	13
20	**13a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/2.5 h	**13b** (70)	tw
21		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/2 h	**13c** (73)[b]	13
22	**14a**	$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/5 min	**14c** (63)[b]	13
23	**15a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/1 min	**15b** (91)	tw
24		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/3 min	**15c** (60)[b]	13
25	**16a**	$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/1 min	**16b** (85)	tw
26		$(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/THF/Δ/16 h	**16b** (72)	tw
27		$(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$	Pd(TPP)$_4$/DMF/150 °C/3 min	**16c** (63)[b]	13

[a] tw = this work. [b] Product resulting from the homocoupling of the triflate (<10%) was detected. [c] (*Z*/*E*) = 70/30. [d] Yield from (*E*)-**9a**.

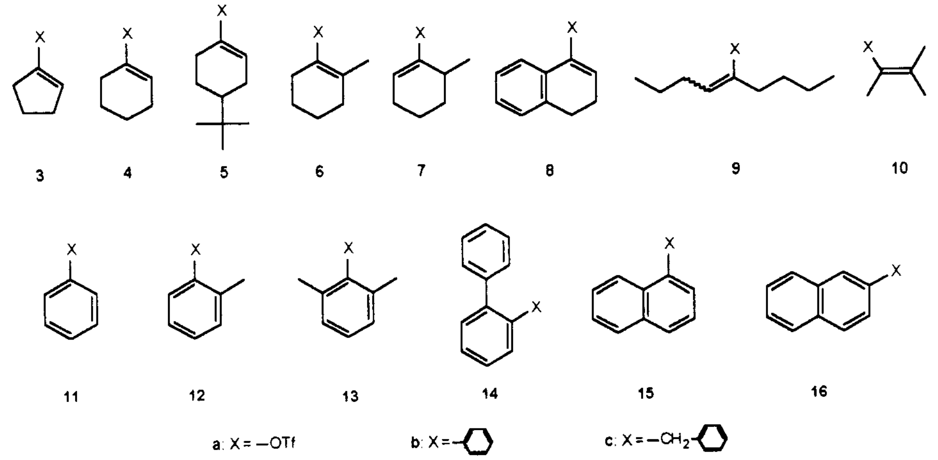
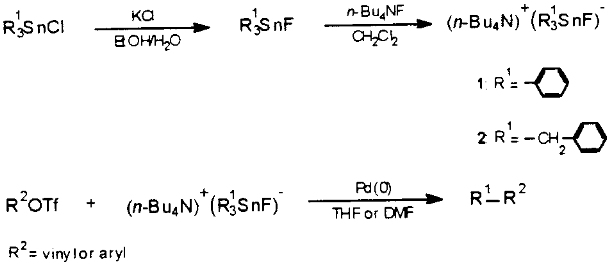


Figure 1. Starting triflates and coupling products.

Scheme 1. Reaction of Vinyl and Aryl Triflates with Hypervalent Organotin Reagents



anion to form strong bonds with tin.[16] Clear evidence of the formation of complex **2** is given by ^{19}F NMR. The spectrum of **2** shows a signal at −156.7 ppm, $J(^{19}\text{F}-^{119}\text{Sn}) = 1598$ Hz, $J(^{19}\text{F}-^{117}\text{Sn}) = 1527$ Hz, a value very similar to the one reported for the pentacoordinated anion $\text{Ph}_3\text{SnF}_2^-$, −160.6 ppm, $J(^{19}\text{F}-^{119}\text{Sn}) = 1944$ Hz.[15,16]

We describe herein new results that complete our previous study about reactions of vinyl and aryl triflates with hypervalent tin reagents. The triflates chosen as well as the yields and reaction conditions of the couplings carried out are listed in Figure 1 and Table 1. We have centered our interest on the arylation and

---

(14) In the meantime, some other examples of Pd(0) cross-coupling reactions of hypervalent tin reagents have been described. For the fluoride-activated reactions of monoorganotins with aryl and vinyl iodides and benzylic bromides, see: (a) Fouquet, E.; Pereyre, M.; Rodriguez, A. L. *J. Org. Chem.* **1997**, *62*, 5242. (b) Fouquet, E.; Rodriguez, A. L. *Synlett* **1998**, 1323. For reactions of aryl bromides and iodides with tetraorganotins and n-Bu$_4$NF, see: (c) Fugami, K.; Ohnuma, S.; Kameyama, M.; Saotome, T.; Kosugi, M. *Synlett* **1999**, 63. For reactions of aryl chlorides with tetraorganotins and CsF, see: (d) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2411. Also hypervalent silicon and boron reagents have been employed in Pd(0)-catalyzed cross-coupling reactions. For procedures involving hypervalent silicon compounds, see: (e) Mowery, M. E.; DeShong, P. *Org. Lett.* **1999**, *1*, 2137. (f) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 1684. (g) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 3266. (h) Matsuhashi, H.; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jp.* **1997**, *70*, 437. (i) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845. For fluoride-mediated boronic acid cross-coupling reactions, see: (j) Wright, S. W.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095.

benzylation of aryl and vinyl triflates due to the limitations of the Stille procedure in these cases (vide supra).

Arylation of Vinyl and Aryl Triflates. The results of the arylation of vinyl triflates are listed in Table 1 (entries 1−6, 9, 11, 13, and 14). Since organostannate **1** can be also prepared in situ, we have tested different reaction conditions differing in the generation of the hypervalent reagent (entries 2−6). The best results are obtained with the salt $(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$ (**1**) (83%) and the mixture $\text{Ph}_4\text{Sn}/n\text{-Bu}_4\text{NF}$ (85%). The yields are comparable, but in the last case a larger amount of reagents is necessary (2 equiv). Therefore, **1** was used in all further assays.

As can be seen, both vinyl and aryl (entries 17, 20, 23, 25, and 26) triflates undergo cross-coupling arylation with **1** in very short reaction times (30 min for vinyl triflates and 1 min to 2.5 h for aryl triflates). The lower rate in the arylation of triflate **13** is probably due to the steric hindrance of the *ortho* methyl groups. The best results are obtained when THF is employed for the arylation of vinyl triflates (81−85%) and DMF for the arylation of aryl triflates (56−91%). It is noteworthy that addition of LiCl is not necessary to achieve the substitution of the triflate group by hypervalent organotins, while in the Stille reaction, the presence of LiCl is often a requisite to induce the coupling of organic triflates.[1a] The arylation of vinyl triflates takes place regiospecifically (entries 9 and 11) as well as stereospecifically (entry 14). In the reaction of both vinyl and aryl triflates, a small amount (<10%) of biphenyl derived from the homocoupling of the stannate is usually obtained.

Benzylation of Vinyl and Aryl Triflates. First attempts to extend the reaction conditions for the arylation of vinyl triflates to the benzylation with **2** were unsuccessful, because complicated mixtures of products were obtained. Similar negative results were reached by preparing **2** in situ by mixing Bn_3SnF, $n\text{-Bu}_4\text{NF}$, and the vinyl triflate in different ratios (triflate/$\text{Bn}_3\text{SnF}/n\text{-Bu}_4\text{NF}$: 1/2/4, 1/2/2, or 1/1/1). Fortunately, this obstacle could be overcome (entries 7, 8, 10, 12, 15, and 16) using reagent **2** under the same reaction conditions as for the benzylation of aryl triflates (entries 18, 19, 21, 22, 24, and 27), changing only the solvent from THF to DMF. The best results were obtained introducing the reaction mixture in an oil bath heated at the temperatures indicated in Table 1. Under these conditions, benzylations takes place in very short times, in some cases nearly instantaneously (entries 10, 12, 15, and 16), in moderate to good yields. Higher temperatures and longer reaction times lower the yield. The kinetically controlled reaction of triflate **7a** (entry 12) affords only 40% of the coupling product, a low yield in comparison to triflate **6a** (73%, entry 10). The reason for this could be decomposition of **7a** during isomerization to the more stable triflate **6a** under the reaction conditions.

It should be noted that in the reactions of the acyclic vinyl triflates (*Z*)-**9a** and (*E*)-**9a** (entry 15) the reaction takes place with formation of only the (*E*) isomer from a mixture of (*Z*)/(*E*)-**9a**. This result is due to the elimination of TfOH from the acyclic triflates, particularly in the case of (*Z*)-**9a**, whose *anti* elimination is favored. Analogous side reactions were described in the case of the Stille cross-coupling reactions of acyclic triflates.[1a] However, the phenylation of triflate **9a** takes place without elimination and, therefore, with high yields.[12]

Stannate **2** also reacts with aryl triflates in DMF to afford the corresponding diarylmethanes in good yield (entries 18, 19, 21, 22, 24, and 27).[13] As in the benzylation of vinyl triflates, reaction times are very short (1 min to 2 h). To achieve high yields, the reaction mixture should be introduced in a preheated (150 °C) oil bath. To test the validity of this benzylation procedure, we carried out the reaction of triflate **11a** with BnSnBu_3 and Pd(TPP)/LiCl, obtaining 20% of the corresponding reaction product only. Besides this, no coupling was observed following the procedure described in the literature based on activated monoorganotins.[14a,b]

Addition of LiCl in benzylation of both vinyl and aryl triflates is not necessary. Small amounts (<10%) of homocoupling products derived from **2** are detected in all reactions.

Conclusions

In this work we have shown that Pd(0) cross-coupling reaction of hypervalent tin reagents **1** and **2** with vinyl and aryl triflates represents an important improvement over the classical Stille reaction, mainly in those cases were this method fails. The couplings with **1** and **2** take place in very short reaction times, and addition of LiCl is not necessary. The reactions described by us are good procedures for the preparation of biaryls[17] and diphenylmethanes.[11,18] Extension of the scope of this method to other classes of stannates and electrophiles as well as study of the tolerance to functional groups on the stannate and the triflate are currently under investigation.

Experimental Section

General Information. All starting materials and reagents were obtained from well-known commercial supplies and were used without further purification. THF and hexane were dried by distillation over sodium/benzophenone and DMF over calcium hydride, under a positive pressure of Ar, immediately prior to use. All reactions were carried out under an Ar atmosphere. Flash chromatography was performed over silica gel (230−400 mesh). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a 300 MHz spectrometer for ^{1}H, on a 75 MHz spectrometer for ^{13}C, and on a 235 MHz spectrometer for ^{19}F. Chemical shifts (δ) for ^{1}H, ^{13}C, and ^{19}F NMR were recorded in ppm downfield relative to the internal standard tetramethylsilane (TMS) for ^{1}H and ^{13}C and external $\text{CF}_3{-}\text{C}_6\text{H}_5$ for ^{19}F NMR. Coupling constants (*J*) are in Hz. IR spectra were recorded in a FT spectrometer. Wavenumbers are in cm^{-1}. Mass spectra were recorded on a 60 eV mass spectrometer.

---

(15) (a) Gingras, M. *Tetrahedron Lett.* **1991**, *32*, 7381. (b) Jang, M.; Janzen, A. F. *J. Fluorine Chem.* **1994**, *66*, 129.

(16) Gingras, M.; Chan, T. H.; Harpp, D. N. *J. Org. Chem.* **1990**, *55*, 2078.

(17) For a review on the synthesis of biaryls, see: Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263.

(18) Some procedures for the preparation of diphenylmethanes are described in: (a) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron Lett.* **1998**, *39*, 6291. (b) Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukuzawa, S. *J. Org. Chem.* **1997**, *64*, 66997. (c) Kim, S.-H.; Rieke, R. D. *J. Org. Chem.* **1998**, *63*, 6766. (d) Rottländer, M.; Knochel, P. *Tetrahedron Lett.* **1997**, *38*, 1749. (e) Ku, Y.-Y.; Patel, R. R.; Sawick, D. P. *Tetrahedron Lett.* **1996**, *37*, 1949. (f) Yamato, T.; Sakane, N.; Suehiro, K.; Tashiro, M. *Org. Prep. Proc. Int.* **1991**, *23*, 617.

Vinyl and aryl triflates were prepared by reaction of the corresponding ketones and phenols with trifluoromethanesulfonic anhydride following procedures described in the literature.[1b,19] Thermodynamic and kinetic control triflates **6a** and **7a** were obtained by means of selective enolization of 2-methylcyclohexanone.[1b,3,20] $(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$ (**1**) is commercially available and can also be obtained by reaction of Ph_3SnF and $n\text{-Bu}_4\text{NF}$ according to the literature.[15] Tribenzyltin chloride[21] and tribenzyltin fluoride[15,22] were obtained following procedures reported in the literature. Benzyltributyltin was prepared by reaction of benzylmagnesium bromide with tributyltin chloride.[23]

Synthesis of Tetrabutylammonium Difluorotribenzylstannate $[(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-]$ (2). A 14.20 g (34.6 mmol) sample of tribenzyltin fluoride was added over a solution of 9.04 g (34.6 mmol) of tetrabutylammonium fluoride in 400 mL of CH_2Cl_2. After stirring at 25 °C for 30 min, the solvent was evaporated and the resulting oil was vacuum-dried (0.1 Torr/25 °C). The resulting white, hygroscopic, and low melting point solid was used without further purification. IR (KBr): ν 3078, 3057, 3022, 1599, 1491, 1472, 1452 cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.14−6.87 (m, 15H), 3.12−2.97 (m, 8H), 2.38 (s, 6H, $^2J(^1\text{H}-^{119}\text{Sn}) = 92$ Hz), 1.59−1.23 (m, 16H), 0.98 (t, 12H, $J = 7.1$ Hz) ppm. ^{13}C NMR (CDCl_3): δ 142.6, 128.5, 127.8, 123.0, 58.6, 28.5($^1J(^{13}\text{C}-^{119}\text{Sn}) = 523$ Hz), 23.9, 19.7, 13.7 ppm. ^{19}F NMR (CDCl_3): δ −156.7 ppm, $J\,(^{19}\text{F}-^{119}\text{Sn}) = 1599$ Hz, $J\,(^{19}\text{F}-^{117}\text{Sn}) = 1527$ Hz.

General Procedure for the Arylation of Vinyl Triflates. A solution of 1.8 mmol of the alkenyl triflate, 1.8 mmol of $(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$ (**1**), and 0.18 mmol of Pd(TPP)_4 in 30 mL of anhydrous THF was refluxed under argon atmosphere for 30 min. After cooling, 70 mL of dichloromethane was added and the resulting solution washed with water (2 × 50 mL), filtered through Celite, and dried over magnesium sulfate. The alkenylbenzenes were purified by column chromatography (silica gel, hexane).

General Procedure for the Arylation of Aryl Triflates. Over a solution of 1.30 mmol of the aryl triflate in 5 mL of DMF (5 mL of THF for triflate **11a**) were added, under Ar atmosphere, 1.23 g (1.95 mmol) of $(n\text{-Bu}_4\text{N})^+(\text{Ph}_3\text{SnF}_2)^-$ (**1**) and 0.13 mmol of Pd(TPP)_4. The reaction mixture was then introduced in an oil bath heated at 150 °C during the time indicated in Table 1. After cooling, 25 mL of dichloromethane was added and the resulting solution washed with water (2 × 25 mL) and saturated NaHCO_3 solution (2 × 25 mL) and dried over magnesium sulfate. The solvent was evaporated at reduced pressure, and the arylbenzenes were purified by column chromatography (silica gel, hexane).

General Procedure for the Benzylation of Vinyl Triflates. A mixture of 1.3 mmol of vinyl triflate, 1.05 g (1.6 mmol) of $(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$ (**2**), and 0.13 mmol of Pd(TPP)_4 in 5 mL of DMF was introduced, under argon atmosphere, in an oil bath and heated at the temperature and during the time indicated for each case in Table 1. The reaction mixture was poured into water (50 mL) and extracted with Cl_2CH_2 (3 × 25 mL). The organic solution was washed with water and saturated NaHCO_3 solution and dried over magnesium sulfate. Evaporation of the solvent and purification of the residue by flash chromatography (silica gel, hexane) yielded the corresponding reaction products.

General Procedure for the Benzylation of Aryl Triflates. A solution of 1.3 mmol of aryl triflate, 1.31 g (1.95 mmol) of $(n\text{-Bu}_4\text{N})^+(\text{Bn}_3\text{SnF}_2)^-$, and 0.13 mmol of Pd(TPP)_4 in 6 mL of DMF was introduced, under argon atmosphere, in an oil bath heated at 150 °C. After the reaction time indicated in Table 1, the reaction mixture was poured into water (50 mL) and extracted with Cl_2CH_2 (3 × 25 mL). The organic solution was washed with water and saturated NaHCO_3 solution and dried over MgSO_4. Evaporation of the solvent and purification of the residue by flash chromatography (silica gel, hexane) yielded the corresponding arylphenylmethanes.

Acknowledgment. We thank the DGICYT, Spain (Grant PB-97-0268-C02), for financial support. M.R.C.H. thanks the Universidad Complutense de Madrid and A.F.C. thanks the Comunidad Autónoma de Madrid for grants.

Supporting Information Available: A listing of IR and NMR data of compounds **3b**−**16b** and **3c**−**16c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000957A

---

[19] (a) García Martínez, A.; Subramanian, L. R.; Hanack, M. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley: Chichester, 1995; Vol. 7. (b) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 55.

[20] (a) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979. (b) Crisp, G. T.; Scott, W. J. *Synthesis* **1985**, 335.

[21] Sisido, K.; Takeda, Y.; Kinigawa, Z. *J. Am. Chem. Soc.* **1961**, *83*, 583.

[22] Liebner, J. E.; Jacobus, J. *J. Org. Chem.* **1997**, *64*, 4449.

[23] Eisch, J. J. *Organometallic Syntheses, vol. 2, Nontransition-Metal Compounds*; Academic Press: New York, 1981.