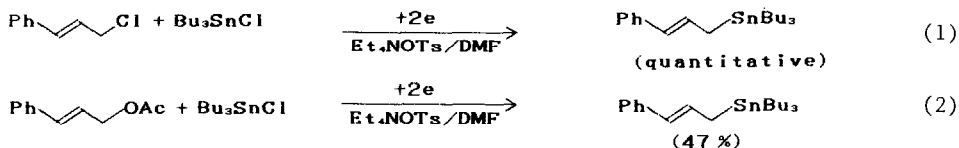


PALLADIUM-CATALYZED COUPLING OF ELECTROGENERATED ALLYL TIN REAGENTS

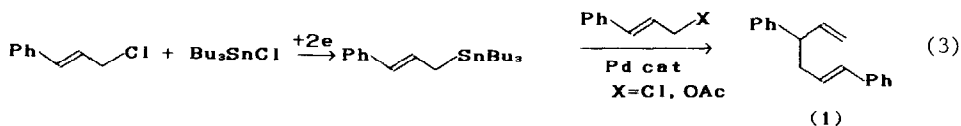
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**Summary:** Palladium-catalyzed homocoupling of allylic halides and acetates under in situ electrochemical generation of the allyl tin reagent was developed.

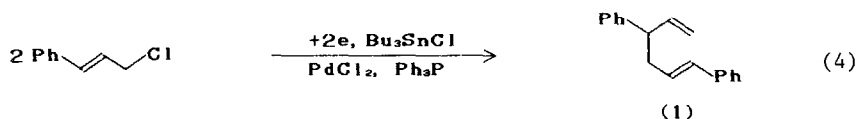
Recently the electrochemical method has been shown to provide a convenient access to organosilicon compounds from organic halides.<sup>2,3</sup> In an effort to expand the scope of the method we examined its applicability to the synthesis of organotin compounds and found that electrochemical reduction of organic halides or acetates in the presence of tributyltin chloride gave the corresponding organotin compounds (eqs 1 and 2).<sup>4</sup>



Synthetic versatility of palladium catalyzed coupling of organotin compounds with organic electrophiles<sup>5</sup> prompted us to combine this electrochemical synthesis of organotin reagents and palladium catalyzed coupling reactions. Thus cinnamyl chloride (1.0 mmol) was electrochemically reduced in the presence of tributyltin chloride (5.0 mmol) in 0.2 M Et<sub>4</sub>NOTs/DMF in a divided cell. After 2.1-2.2 F/mol of electricity based on cinnamyl chloride had been passed, a catalytic amount of palladium chloride (PdCl<sub>2</sub>, 0.02 mmol) and triphenylphosphine (Ph<sub>3</sub>P, 0.11 mmol) was added and ca. 4 F/mol of electricity based on PdCl<sub>2</sub> was passed in order to effect reduction of palladium(II) into low valent palladium species. Then cinnamyl acetate or cinnamyl chloride (0.5 mmol) was added and the mixture was stirred overnight at 50 °C. VPC analysis of the reaction mixture indicated the formation of the coupling product,<sup>6</sup> 1,4-diphenyl-1,5-hexadiene (1) in 60-100% yield based upon the second substrate (eq 3).



Next, we tried to perform palladium catalyzed homocoupling<sup>7,8</sup> under in situ generation of allyltin reagent by the electrochemical method. A mixture of cinnamyl chloride (2 mmol) and tributyltin chloride (5 mmol) in 0.2 M Et<sub>4</sub>NOTs/DMF was electrolyzed in the presence of a catalytic amount of palladium chloride and triphenylphosphine. After 1.14 F/mol of electricity based upon cinnamyl chloride was passed, the electricity was disconnected. At this point VPC analysis indicated the formation of the homocoupling product in about 60% yield, but the reaction mixture was allowed to stand overnight at 50 °C in order to complete the catalytic reaction. 1,4-Diphenyl-1,5-hexadiene (**1**) was then obtained in 89% yield as a single regioisomer (eq 4).



**Table I. Coupling of Cinnamyl Chloride<sup>a</sup>**

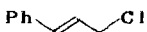
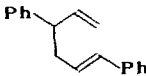
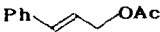
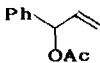
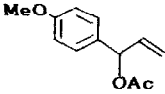
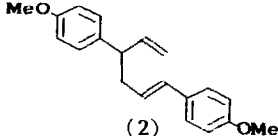
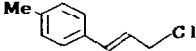
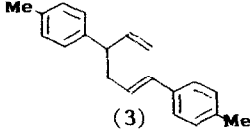
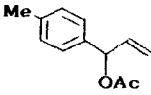
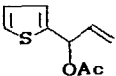
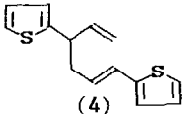
entry	ligand (L)	L/PdCl <sub>2</sub>	electricity (F/mol)	yield of <b>1</b> (%) <sup>b</sup>
1	Ph <sub>3</sub> P	2.19	1.00	92
2		2.24	1.14	89
3		2.12	1.50	69
4		2.44	1.17	63 <sup>c</sup>
5		0.52	1.25	35
6		1.12	1.15	89
7		5.91	1.15	74
8	Bu <sub>3</sub> P	1.92	1.25	28
9	dppp	0.92	1.24	41
10		2.46	1.39	11
11	(EtO) <sub>3</sub> P	2.42	1.25	55

<sup>a</sup> Reactions were normally carried out with cinnamyl chloride (2 mmol), tributyltin chloride (5 mmol), PdCl<sub>2</sub> (0.025 mmol), and a phosphine ligand in 0.2 M Et<sub>4</sub>NOTs/DMF at 50 °C. After constant current (10 mA) was passed, the reaction mixture was allowed to stand overnight at 50 °C. <sup>b</sup> Yields were determined by VPC. <sup>c</sup> After electrolysis the reaction mixture was quenched immediately.

Table I summarizes the results obtained under various conditions. Ratio of triphenylphosphine/PdCl<sub>2</sub> affected the yield of the coupling product (entries 2, 5, 6, and 7). Use of 1-2 equivalents of the ligand gave the best results. Several phosphines were examined as the ligand for palladium species and triphenylphosphine proved the best among the examined. Use

of 1,3-bis(diphenylphosphino)propane (dppp) (entries 8 and 9), tributylphosphine (entry 10), triethylphosphite (entry 11) resulted in lower yields of the product. Thus passing of 1-1.15 F/mol of electricity using 1-2 equiv of  $\text{Ph}_3\text{P}$  gave the best results among the examined (entries 1, 2 and 6). It is also worth noting that standing the reaction mixture overnight after the electrolysis increased the yield of the coupling product (entries 2 and 4), indicating that electrochemical reaction was faster than palladium-catalyzed coupling reaction under the conditions.

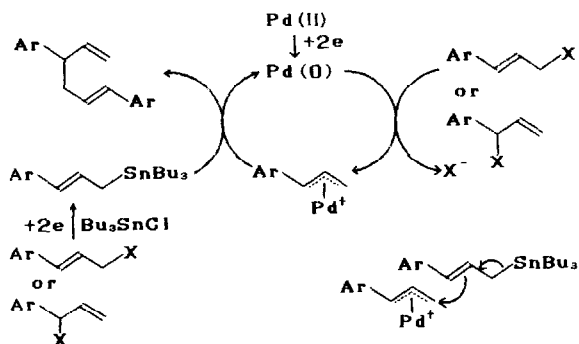
Table II. Homocoupling of Allylic Halides and Acetates<sup>a</sup>

allylic substrate	electricity (F/mol)	product	yield (%) <sup>b</sup>
	1.14	 (1)	89
	1.40	1	82
	1.39	1	79
	1.31	 (2)	42 <sup>c</sup>
	1.15	 (3)	57
	1.40	3	82
	1.16	 (4)	55

<sup>a</sup> Reactions were normally carried out with an allylic substrate (2 mmol), tributyltin chloride (5 mmol),  $\text{PdCl}_2$  (0.025 mmol), and  $\text{Ph}_3\text{P}$  (0.05 mmol) in 0.2 M  $\text{Et}_4\text{NOTs}/\text{DMF}$  at 50 °C. After constant current (10 mA) was passed, the reaction mixture was allowed to stand at 50 °C overnight. <sup>b</sup> Yields were determined by VPC. <sup>c</sup> Isolated yield.

Table II summarizes the results obtained for several allylic substrates. Allylic acetates also served as good substrates for the reaction. Alkyl-substituted allylic substrates such as geranyl acetate did not react smoothly. However, aryl-substituted allylic halides and acetates reacted smoothly to give the corresponding homocoupling products. Regiochemistry of the coupling products did not depend on the regiochemistry of the starting materials. For example, cinnamyl acetate and 3-acetoxy-3-phenylpropene gave the same coupling product as a single regioisomer. The separate experiments revealed that the electrochemical reaction introduces the stannyl group into the less substituted end of the allyl group irrespective of the regiochemistry of the starting materials. Therefore the following mechanism (Scheme I) involving direct attack of allyltin reagent on  $\pi$ -allylpalladium intermediate<sup>6a,6b</sup> seemed to be reasonable.

Scheme I.



## References and Notes

- (1) Present address: Institute of Organic Chemistry, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan.
- (2) Yoshida, J.; Muraki, K.; Funahashi, H.; Kawabata, N. *J. Organomet. Chem.* **1985**, 284 C33.
- (3) Shono, T.; Matsumura, Y.; Katoh, S.; Kise, N. *Chem. Lett.* **1985**, 463.
- (4) Electrochemical generation of allyltin compounds from allyl halides and tin powder has been reported: Uneyama, K.; Matsuda, H.; Torii, S. *Tetrahedron Lett.* **1984**, 25, 6017.
- (5) For example, see: Stille, J. K. *Pure & Appl. Chem.* **1985**, 57, 1771.
- (6) Palladium catalyzed coupling of allyltin reagents with allyl halides or acetates, see: (a) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, 21, 2595. (b) Godschalx, J.; Stille, J. K. *Tetrahedron Lett.* **1980**, 21, 2599. (c) Trost, B. M.; Pietrusiewicz, K. M. *Tetrahedron Lett.* **1985**, 26, 4039.
- (7) Palladium catalyzed homocoupling of allyl acetates using a stoichiometric amount of zinc as a reducing agent has been reported: Sasaoka, S.; Yamamoto, T.; Kinoshita, H.; Inomata, K.; Kotake, H. *Chem. Lett.* **1985**, 315.
- (8) Electrochemical reductive homocoupling of allyl halides using  $\text{Cu}(\text{acac})_2$  as catalyst has been reported: Tokuda, M. Satoh, K.; Suginome, H. *Chem. Lett.* **1984**, 1035.

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