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A coupling reaction of aryltributyltin with olefins mediated by palladium(II) acetate

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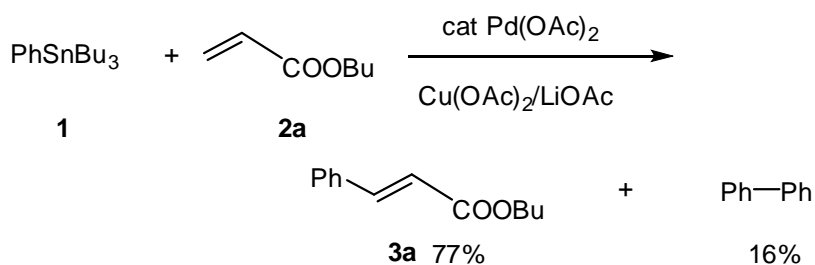
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Abstract: Phenyltributyltin is found to react with butyl acrylate in the presence of Pd(OAc)₂ (10 mol%), Cu(OAc)₂ (3 mol), and LiOAc (2 mol) in DMF to afford butyl 3-phenylpropenoate in 77% yield. Methyl vinyl ketone, acrolein, acrylonitrile, and styrene are also applicable to this reaction as a substrate.

The Mizoroki-Heck (M-H) reaction serves as one of the significant method for carbon-carbon bond formation at an *sp*² carbon starting with an organic halide and an olefin.¹ Although, the use of organometallic or -metalloid reagents instead of the organic halides is also a method of choice, such reactions have not well been studied.² The M-H type reaction with organotin compounds in the presence of a stoichiometric amount of palladium(II) was documented in 1969 by Heck, the reactivity of the tin reagent was reported therein to be inferior to organomercury reagents.^{2e} The reactions of organotin reagents to an olefinic compound have little been studied thereafter,³ in contrast with numerous studies for the Migita-Stille coupling, one of the most practical cross-coupling reactions.⁴

On the other hand, we recently disclosed that the reaction of aryl- and alkenylsilanols, a typical example of the metalloid reagent, with several olefins afforded the identical product with M-H reaction⁵ in the presence of Cu(II) salt and a catalytic amount of palladium(II) acetate. These findings prompted us to investigate a possibility of such reactions with organotin compounds. We herewith wish to describe that organotin compounds are also an appropriate organometalloid reagent to effect the palladium catalyzed Mizoroki-Heck type coupling reaction with olefins.

When the reaction was carried out with phenyltributyltin (**1**, 1 mmol) with butyl acrylate (**2a**, 1 mmol) under the conditions for silanols [Pd(OAc)₂ (10 mol%), Cu(OAc)₂ (3 mmol), and LiOAc (2 mmol) in DMF, 100 °C, 24 h], butyl 3-phenylpropenoate (**3a**) was obtained in 77% yield along with biphenyl (16% yield), a homo-coupled product of **1**.⁶

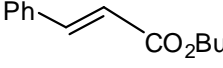
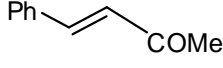
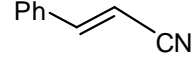
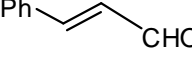
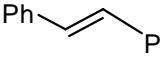
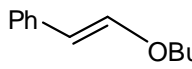
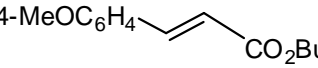
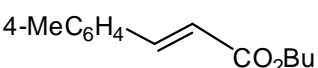
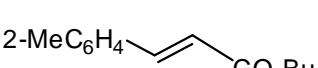
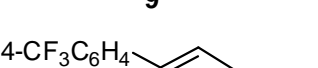


Scheme 1

Organotin compound **1** was also found to react with electron-deficient terminal olefins such as acrylates, acrylonitrile, methyl vinyl ketone and acrolein to give the M-H products in good yields as summarized in Table 1. Styrene also underwent the reaction to give *trans*-stilbene in 73% yield. An electron-rich olefin like butyl vinyl ether turned out to be much less reactive. In addition, variously substituted phenyltributyltins also effected the reactions. However, alkenyl- and alkynyltributyltin compounds underwent a homo-coupling to afford conjugated dienes and diynes, respectively. Tetrabutyltin could not transfer a butyl group to acrylate **2a**.

It is remarkable that the reaction of aryltin compounds proceeded cleanly compared with that of silanols to afford the corresponding products along with a small amount of the homo-coupled biaryls and none of unidentified byproducts. However, prolonged exposure of the aryltributyltin to the palladium catalyst was found to enhance the yield of the undesired homo-coupled product, which, in contrast, was rarely observed in the coupling reaction of silanols under the similar conditions. Indeed, when **10** was stirred at room temperature for 5 min with 10 mol% of Pd(OAc)₂, Cu(OAc)₂, and LiOAc prior to the addition of **2a**, the yield of biaryl was increased to 72% and the yield of **11** was decreased to 8% (see entry 10 of Table 1: the result for the immediate addition of **2a** to the reaction system).

Table 1. Reaction of aryl(tributyl)tin reagents with an olefin in the presence of Pd(OAc)₂.^a

Entry	R	R'	Product	Yield (%)
1	Ph	CO ₂ Bu		77 ^b
	1	2a	3a	
2		COMe		64 ^b
		2b	3b	
3		CN		59 ^c
		2c	3c	
4		CHO		58
		2d	3d	
5		Ph		73 ^b
		2e	3e	
6		OBu		8 ^{b, d}
		2f	3f	
7	4-MeOC ₆ H ₄	2a		60
	4		5	
8	4-MeC ₆ H ₄	2a		86
	6		7	
9	2-MeC ₆ H ₄	2a		71
	8		9	
10	4-CF ₃ C ₆ H ₄	2a		50 ^e
	10		11	

^aThe reaction conditions are described in the general procedure unless otherwise specified. ^bTin compound used were 0.3 mmol.

^cE/Z = 76/24 by ¹H NMR. ^dOther product: Ph-Ph (90%).

^eA byproduct (4-CF₃C₆H₄)₂ 41%.

We understand the reaction mechanism in terms of the following 3 steps: (i) transmetalation of an aryl group from tin to Pd(II), (ii) insertion of a terminal olefin to a Pd(II)-carbon bond, (iii) a β -hydride elimination to give the corresponding product and Pd(0), which is oxidized to Pd(II) by a Cu(II) salt as was the case of the Wacker process.⁷ Indeed, in the absence of copper(II) acetate, the reaction of Scheme 1

using $\text{Pd}(\text{OAc})_2$ (20 mol% or 100 mol%) in DMF at 100 °C for 3 days gave **3a** in 8 or 60% yield, respectively.

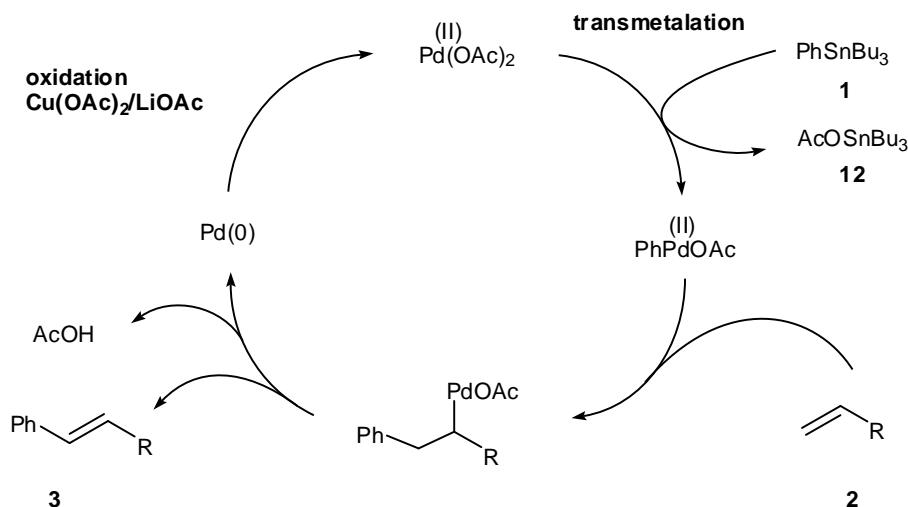


Fig. 1 The reaction of phenyltributyltin and an olefin with $\text{Pd}(\text{OAc})_2$.

An alternative mechanism was suggested for the similar reaction using an organoboronic acid by Cho and Uemura,^{2c} who described that the initial step of the catalytic cycle is an oxidative addition of $\text{Pd}(0)$ to the carbon-boron bond. Since an organotin reagent, in general, is shown to exhibit divergent characters toward the reactions of palladium species, the oxidative addition to $\text{Pd}(0)$ ⁸ and the transmetalation with $\text{Pd}(II)$,⁹ the reaction pathway involving the oxidative addition might also be possible. However, treatment of **1** with **2a** in the presence of a $\text{Pd}(\text{OAc})_2$ catalyst in AcOH/AcONa , the similar conditions of Cho and Uemura, gave no trace of **3a**. Thus, the mechanism involving the oxidative addition is unlikely in the reaction of the aryltin reagent.

The transmetalation mechanism illustrated in Fig 1 suggests that Bu_3SnOAc (**12**) should be produced along with a Ph-Pd species from **1** and $\text{Pd}(\text{OAc})_2$. Indeed, ^1H and ^{119}Sn NMR spectra of a reaction mixture in $\text{DMF-}d_7$ showed signals at 1.93 ppm (^1H) and 7.7 ppm (^{119}Sn), respectively, both ascribed to **12** in AcOH .¹⁰

In summary, aryltributyltins are found to undergo the M-H type reaction with a variety of olefins as observed with arylsilanols, arylboronic acids, and aryl halides. In particular, the reaction of tin reagents was suggested to proceed through a transmetalation in a manner similar to silanols but in contrast to boronic acids or aryl halides.

Acknowledgement. We are indebted to Professor Masanori Kosugi and Dr. Keigo Fugami of Gunma University for helpful discussion.

General procedure for the coupling reaction of aryltin reagent with olefin: To a solution of $\text{Pd}(\text{OAc})_2$ (0.03 mmol), $\text{Cu}(\text{OAc})_2$ (0.9 mmol) and LiOAc (0.6 mmol) in DMF (2 mL) placed in a screw capped sealed glass tube were added successively butyl acrylate **2a**

(0.32 mmol) and phenyltributyltin **1a** (0.3 mmol) at room temperature under argon. The mixture was heated with stirring at 100 °C for 24 h and then, after cooling, passed through a Celite pad with diethyl ether (30 mL) as an eluent. The eluate was washed with 1 M HCl aq. (15 mL), sat. NaHCO₃ aq. (2 X 15 mL), 5% NH₃ aq. (3 X 100 mL), and brine (20 mL). The ethereal solution was dried over MgSO₄ and concentrated under reduced pressure to leave a crude oil, which was purified by flash column chromatography on silica gel (hexanes/AcOEt = 10/1) to give **3a** in 77% yield.

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References and Notes

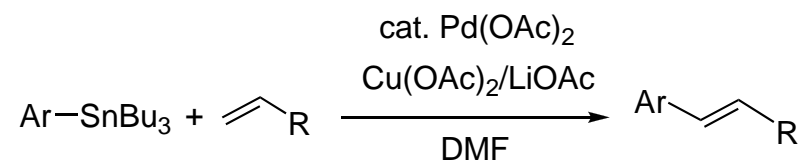
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Graphical abstract

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Mizoroki-Heck type reaction, aryltin compounds,
palladium(II)acetate, copper(II) acetate, lithium acetate



R : CO₂R', COMe, CHO, CN, Ph