A Coupling Reaction of Aryltributyltin with Olefins Mediated by Palladium(II) Acetate

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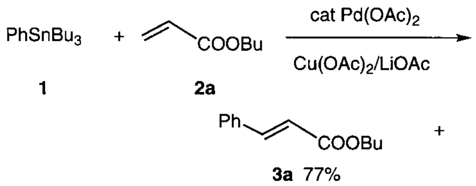
Abstract: Phenytributyltin is found to react with butyl acrylate in the presence of $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (3 mol), and LiOAc (2 mol) in DMF to afford butyl 3-phenylpropenoate in 77% yield. Methyl vinyl ketone, acrolein, acrylonitrile, and styrene are also applicable to this reaction as a substrate.

Key words: Mizoroki-Heck type, aryltin, palladium(II) acetate, copper(II) acetate, lithium acetate



Scheme 1

The Mizoroki-Heck (M-H) reaction serves as one of the significant methods 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 reaction[5] 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 phenytributyltin (**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]

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).

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

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 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 Pd(0)[8] and the transmetalation with Pd(II),[9] the reaction pathway involv-

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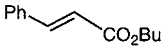
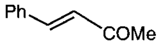
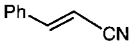
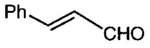
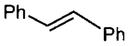
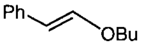
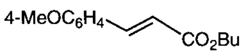
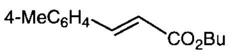
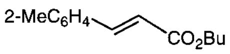
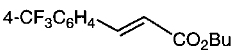
Table 1. Reaction of aryl(tributyl)tin reagents with an olefin in the presence of $Pd(OAc)_2$ [a]

Entry	R	R'	Product	Yield (%)
1	Ph **1**	CO_2Bu **2a**	 **3a**	77^b
2		COMe **2b**	 **3b**	64^b
3		CN **2c**	 **3c**	59^c
4		CHO **2d**	 **3d**	58
5		Ph **2e**	 **3e**	73^b
6		OBu **2f**	 **3f**	$8^{b,d}$
7	$4\text{-}MeOC_6H_4$ **4**	**2a**	 **5**	60
8	$4\text{-}MeC_6H_4$ **6**	**2a**	 **7**	86
9	$2\text{-}MeC_6H_4$ **8**	**2a**	 **9**	71
10	$4\text{-}CF_3C_6H_4$ **10**	**2a**	 **11**	50^e

[a] The reaction conditions are described in the general procedure unless otherwise specified. [b] Tin compound used was 0.3 mmol.
[c] *E/Z* = 76/24 by ^1H NMR. [d] Other product: Ph-Ph (90%).
[e] A byproduct $(4\text{-}CF_3C_6H_4)_2$ 41%

ing the oxidative addition might also be possible. However, treatment of **1** with **2a** in the presence of a $Pd(OAc)_2$ 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 $Pd(OAc)_2$. Indeed, ^1H and ^{119}Sn NMR spectra of a reaction mixture in 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.

General procedure for the coupling reaction of aryltin reagent with olefin: To a solution of $Pd(OAc)_2$ (0.03 mmol), $Cu(OAc)_2$ (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. $NaHCO_3$ aq. (2 x 15 mL), 5% NH_3 aq. (3 x 100 mL), and brine (20 mL). The ethereal solution was dried over $MgSO_4$ 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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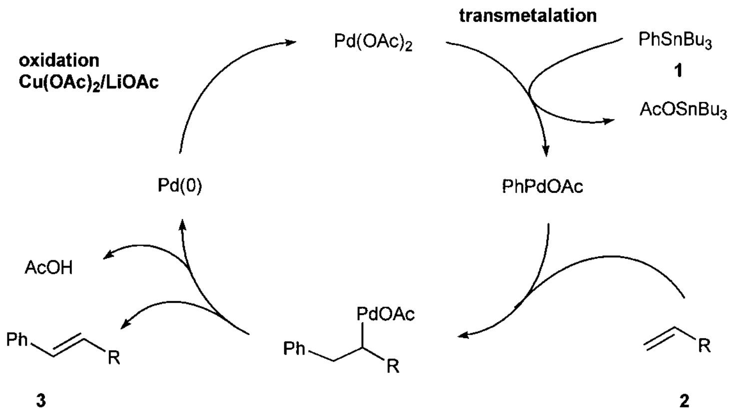

Figure 1. The reaction of phenyltributyltin and an olefin with $Pd(OAc)_2$

References and Notes

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(1) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581. Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1505. Heck, R. F.; Nolley Jr, J. P. *J. Org. Chem.* **1972**, *37*, 2320. Diech, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133. Heck, R. F. *Org. React.* **1982**, *27*, 345.

(2) (a) Murahashi, S.; Yamaura, M.; Mita, N. *J. Org. Chem.* **1977**, *42*, 2870. (b) Luong-Thi, N-T.; Riviere, H. *J. Chem. Soc., Chem. Commun.* **1978**, 918. (c) Cho, C. S.; Uemura, S. *J. Organomet. Chem.* **1994**, *465*, 85. (d) Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542. (e) Heck, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6896. Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 9707.

(3) (a) Oda, H.; Morishita, M.; Fugami, K.; Sano, H.; Koshugi, M. *Chem. Lett*. **1996**, 811. Fugami, K.; Hagiwara, S.; Oda, H.; Kosugi, M. *Synlett* **1998**, 477. (b) Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975. (c) Cassi, S.; Misiti, D. *Tetrahedron Lett*. **1979**, 4591. Oi, S.; Moro, M.; Ono, S.; Inoue, Y. *Chem. Lett.* **1998**, 83.

(4) Kosugi, M.; Sasazawa, K.; Shimizu Y.; Migita, T. *Chem. Lett.* **1977**, 301. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(5) Hirabayashi, K.; Nishihara, Y.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 7893.

(6) Kanemoto, S.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *Chem. Lett.* **1987**, 5. Tolstikof, G. A.; Miftakhov, M. S.; Danilova, N. A.; Vel’der, Y. L.; Spirikhin, L. V. *Synthesis* **1989**, 633. Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434. Alcaraz, L.; Taylor, R. J. K. *Synlett* **1997**, 791.

(7) Tsuji, J. Palladium Reagent and Catalysts; Innovations in Organic Synthesis, Wiley, 1996; p19.

(8) Shi, M.; Nicholas, K. M. *J. Am. Chem. Soc*. **1997**, *119*, 5057. See also: ref (3b)

(9) Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641.

(10) The ^{1}H and ^{119}Sn NMR spectra of tributyltin acetate itself in DMF-d_7 showed the signal at 1.85 ppm (^{1}H NMR; the acetyl proton) and 8.9 ppm (^{119}Sn NMR).