

Syntheses of 1,3- and 1,4-Dienes by the Oxidative Coupling of
1-Alkenylstannanes and 2-Alkenylstannanes in the Presence of Palladium Catalyst[†]

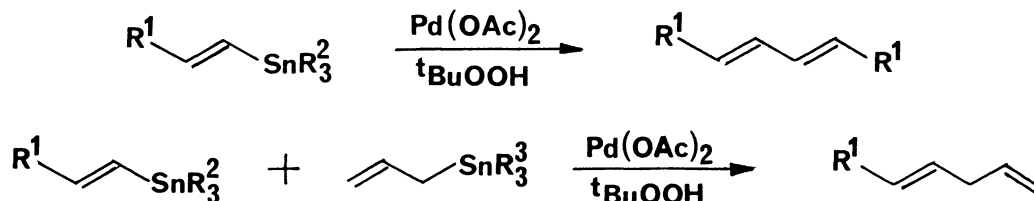
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Treatment of 1-alkenylstannanes with ^tBuOOH in the presence of palladium catalyst gives 1,3-dienes. Cross coupling reaction between 1-alkenylstannanes and 2-alkenylstannanes provides 1,4-dienes selectively in good yields.

The cross coupling of an organotin with an organic halide catalyzed by a transition metal is an important, versatile method of carbon-carbon bond formation.¹⁾ Here we wish to report the oxidative homo- and cross-coupling of 1-alkenylstannanes and 2-alkenylstannanes by means of Pd(OAc)₂-^tBuOOH system.²⁾

Palladium(II) acetate (23 mg, 0.1 mmol) and (E)-4-benzyloxy-1-tributylstannyl-1-butene³⁾ (0.45 g, 1.0 mmol) were combined in benzene (4 cm³). A solution of ^tBuOOH⁴⁾ (3.0 M, 0.67 cm³, 2.0 mmol) in benzene was added and the mixture was stirred at 25 °C for 2 h. The resulting mixture was poured into saturated aq. NaHSO₃ and extracted with AcOEt. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification by silica gel column chromatography gave the corresponding diene, (E,E)-1,8-dibenzyloxy-3,5-octadiene (**1**) (0.12 g) in 77% yield: IR (neat) 2820, 1715, 1445, 1375, 1100, 1025, 985, 730, 695 cm⁻¹; NMR (CCl₄) δ 2.1-2.5 (m, 4H), 3.40 (t, *J* = 6.5 Hz, 4H), 4.40 (s, 4H), 5.30-6.15 (m, 4H), 7.1-7.3 (m, 10H). The representative results are summarized in Table 1 (Entries 1-5).

The reaction of a mixture of 2-alkenylstannanes and 1-alkenylstannanes with Pd(OAc)₂-^tBuOOH gave 1,4-diene selectively along with a small amount of 1,3-dienes derived from homo-coupling of 1-alkenylstannanes. For instance, treatment of a mixture of allyltriethylstannane (2.0 mmol) and (E)-4-benzyloxy-1-tributylstannyl-1-butene (1.0 mmol) with ^tBuOOH (2.0 mmol) in the presence of a catalytic amount of Pd(OAc)₂ (0.1 mmol) gave a mixture of 1-phenyl-1,4-pentadiene (0.14 g, 70%) and the conjugated diene **1** (<5%). 1,5-Hexadiene generated by homo-coupling of 2-alkenylstannanes could not be observed in the reaction mixture.⁵⁾



[†]Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

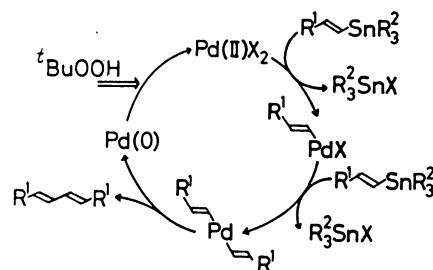
Table 1. Synthesis of 1,3-dienes and 1,4-dienes^{a)}

Entry	Substrate	Product	Yield/% ^{b)}
1			80
2			76
3			77
4			77
5		Ph-Ph	83
6	+		68
7	+		72
8	+		53
			18
9	+		70
10	+		52
			16

a) 1-Alkenylstannane (1.0 mmol), Pd(OAc)₂ (0.1 mmol), and ^tBuOOH (2.0 mmol) were employed for entries 1-5. 2-Alkenylstannane (2.0 mmol), 1-alkenylstannane (1.0 mmol), Pd(OAc)₂ (0.1 mmol), and ^tBuOOH (2.0 mmol) were employed for entries 6-10. b) Isolated yields. c) A mixture of (E,E) isomer and (E,Z) isomer (4:1). d) Only (E,E) isomers were obtained. e) Cross coupling gave (E) isomers exclusively (Entries 6-10).

References

- 1) J. K. Stille, *Pure Appl. Chem.*, **57**, 1771 (1985) and references cited therein; M. Kosugi, I. Hagiwara, and T. Migita, *Chem. Lett.*, **1983**, 839.
- 2) We are tempted to assume the following reaction mechanism for homo-coupling of 1-alkenylstannanes. The double transmetalation followed by reductive elimination gives 1,3-dienes. The deposited palladium(0) is oxidized by ^tBuOOH and recycled.
- 3) S. Matsubara, J. Hibino, Y. Morizawa, K. Oshima, and H. Nozaki, *J. Organometal. Chem.*, **285**, 163 (1984).
- 4) J. G. Hill, B. E. Rossiter, and K. B. Sharpless, *J. Org. Chem.*, **48**, 3607 (1983).
- 5) Treatment of 2-alkenylstannanes with our system resulted in the recovery of the starting materials. Schwartz et al. have reported that bis(allylic)-palladium complexes do not provide 1,5-dienes in the absence of a π-acidic ligand such as maleic anhydride. A. Gollaszewski and J. Schwartz, *Organometallics*, **4**, 417 (1985).



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