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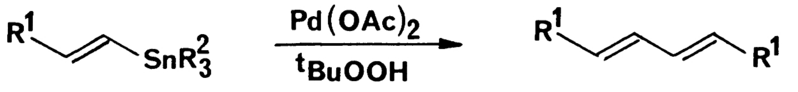
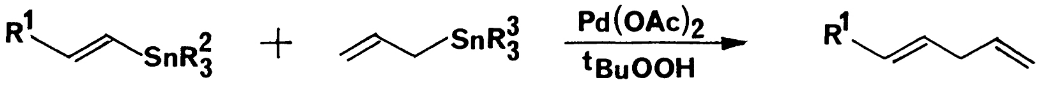
Treatment of 1-alkenylstannanes with ^{t}BuOOH in the presence of palladium catalyst gives 1,3-dienes. Cross coupling reaction between 1-alkenylstannanes and 2-alkenylstannanes provides 1,4-dienes selectively in good yields.

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 $Pd(OAc)_2$-^{t}BuOOH 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 cm^3). A solution of ^{t}BuOOH4) (3,0 M, 0.67 cm^3, 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. $NaHSO_3$ and extracted with AcOEt. The combined organic layers were washed with brine, dried over Na_2SO_4, 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 (CCl_4) 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 $Pd(OAc)_2$-^{t}BuOOH 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 ^{t}BuOOH (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)





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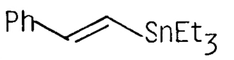
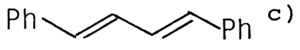
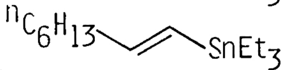
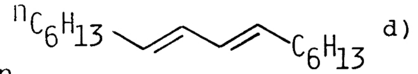
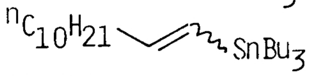
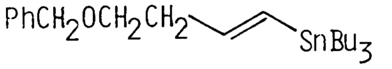
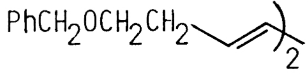
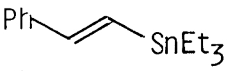
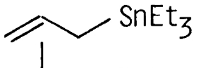
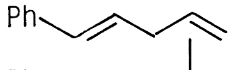
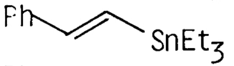
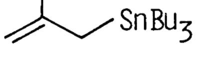
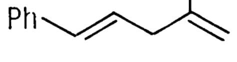
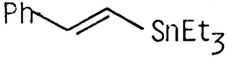
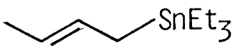
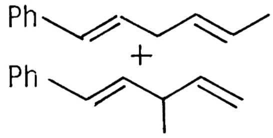
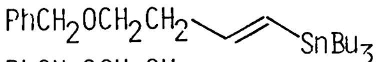
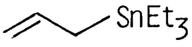
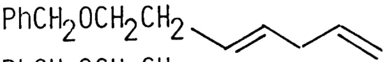
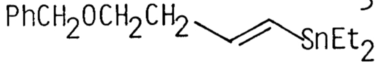
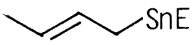
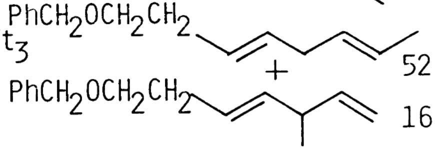
†Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

Table 1. Synthesis of 1,3-dienes and 1,4-dienes[a]

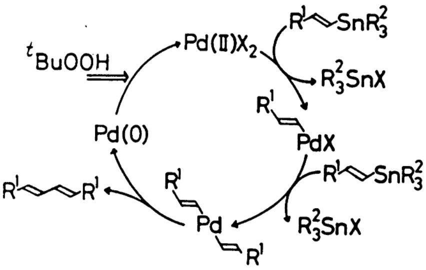
Entry	Substrate		Product	Yield/%[b]
1			 [c]	80
2			 [d]	76
3				77
4			 (1)[d]	77
5	$PhSnBu_3$		Ph-Ph	83
6			 [e]	68
7				72
8				53 18
9				70
10				52 16

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 transmetallation 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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