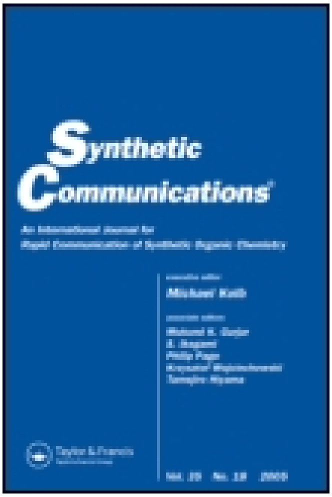

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Reductive Coupling Reaction of Hypervalent Iodonium Salts Catalyzed by Palladium-Zinc System

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REDUCTIVE COUPLING REACTION OF HYPERVALENT IODONIUM SALTS CATALYZED BY PALLADIUM-ZINC SYSTEM

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Abstract: The ligand coupling of various diaryl- or alkynyl(phenyl)iodonium salts in the presence of diethylzinc and a palladium catalyst afforded biaryls or dialkynes under mild conditions.

Symmetrical and unsymmetrical biaryl compounds are structural features of a variety of biologically active natural products[1] and show specific properties as materials to form semiconducting charge transfer complexes[2] and optically active ligands.[3] The reductive coupling of haloarenes catalyzed by copper compounds have been known to give biaryls in the Ullmann reaction.[4] Also, the Kharasch-type cross-coupling reactions of an aromatic Grignard

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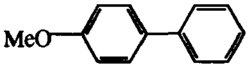
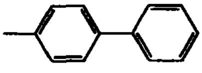
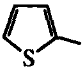
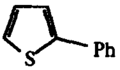
reagent with an aryl halide by nickel(II), palladium(II), or other reagents.[5] The direct synthesis of biaryls from aryl halides can be achieved by transition metal catalysis in the presence of a reductant. Thus, the synthesis of biaryls from aryl halides catalyzed by nickel(II) complexes in the presence of a chemical reductant such as zinc powder or upon electrochemical reduction has been known.[6] Tamura et al.[7] reported that the substituted diaryldiazonium bromides react with a Grignard reagent in the presence of $NiCl_2$ as catalyst to give mixtures of biaryls. The reductive coupling of diaryl iodonium bromides or iodides catalyzed by palladium and Zn was reported by Yamazaki et al.[8] Here we wish to report the reductive coupling of various diayl- or alkynyl(phenyl)iodonium tetrafluoroborate and triflate in the presence of palladium catalyst and diethylzinc(Eq.1).

$$R_1R_2I^+X^- \xrightarrow[Et_2Zn]{\text{Pd-catalyst}} R_1-R_2$$

The result of the reductive coupling of hypervalent iodonium salts in the presence of palladium catalyst and diethylzinc is summarized in Table 1. The iodonium salt **1a** was subjected to react with a catalytic amount of $Pd(OAc)_2$ in the pressure of diethylzinc at room temperature for 30 min to afford biphenyl (**2a**) in 80% yield (entry 1). When $Pd(acac)_2$ was used instead of $Pd(OAc)_2$, biphenyl (**2a**) was afforded in a comparable yield (entry 2). This method was extended to alkynyl-substituted iodonium tetrafluoroborate **1b** and diacetylene **2b** was obtained (entry 3). The aryl-substituted phenyliodonium triflates **1c**

Table 1. The Reductive Coupling of Hypervalent Iodonium Tetrafluoroborates and Triflates

Entry	Iodonium Salts[a]	Catalyst	Zn	Product	Isolated Yield(%)[b]
1	$Ph_2I^+ BF_4^-$ **1a**	$Pd(OAc)_2$	Et_2Zn	Ph-Ph **2a**	80
2	**1a**	$Pd(acac)_2$	Et_2Zn	**2a**	76
3	$Ph{-}\equiv{-}I^+Ph\ BF_4^-$ **1b**	$Pd(OAc)_2$	Et_2Zn	$Ph{-}\equiv{-}\equiv{-}Ph$ **2b** Ph-Ph	52 20
4	*p*-$MeOC_6H_4I^+Ph\ ^-OTf$ **1c**	$Pd(OAc)_2$	Et_2Zn	 **2c** Ph-Ph	46 48
5	*p*-$MeC_6H_4I^+Ph\ ^-OTf$ **1d**	$Pd(OAc)_2$	Et_2Zn	 **2d**	68
6	 $I^+Ph\ ^-OTs$ **1e**	$Pd(OAc)_2$	Et_2Zn	 **2e**	74

[a] The iodonium salts were prepared by Ochiai's procedure. [b] The yields are isolated yields.

and **1d** were also treated with a catalytic amount of $Pd(OAc)_2$ (5 mol %) in the presence of Et_2Zn (2 equiv) to provide methoxy- or methyl-substituted biphenyls **2c** and **2d** in 46 and 68% yields, respectively (entries 4 and 5). Finally, the reaction of 2-thienyl-substituted phenyliodonium tosylate **1e** to afford 2-phenyl-substituted thiophene **2e** (entry 6).

Experimental Section

Typical Procedure: Biphenyl(2a).

To a stirred solution of diphenyliodonium tetrafluoroborate(100 mg, 0.27 mmol) and $Pd(OAc)_2$(6 mg, 5 mol %) in THF(10 mL) was added diethylzinc(1 M, 0.52 ml, 0.52 mmol). The reaction mixture was stirred at room temperature for 30 min and then extracted with ether(2 X 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography(hexanes, R_f = 0.50) to give **2a**(16.6 mg, 80%). TLC, SiO_2, hexanes, R_f= 0.50. IR(KBr) 3060, 1608, 1475, 831 cm^{-1}. ^1H NMR($CDCl_3$, 400 MHz) δ 7.35(m, 2H), 7.45 (m, 4H), 7.61(m, 4H). MS(m/e) 154(M^+, base peak), 152, 77, 76.

1,4-Diphenylbutadiyne(2b): TLC, SiO_2, hexanes, R_f = 0.38. IR(KBr) 3150, 2150, 695 cm^{-1}. ^1H NMR($CDCl_3$, 400 MHz) δ 7.30(m, 6H), 7.50(m, 4H). MS(m/e) 202(M^+, base peak), 101, 77.

4-Methoxy-1,1'-biphenyl(2c): TLC, SiO_2, hexanes, R_f = 0.17. IR(KBr) 3055, 1605, 1265 cm^{-1}. ^1H NMR($CDCl_3$, 400 MHz) δ 3.87(s, 3H), 7.01(m, 1H), 7.34(m, 1H), 7.45(m, 2H), 7.58(m, 4H). MS(m/e) 184(M^+, base peak), 169, 77.

4-Methyl-1,1'-biphenyl(2d): TLC, SiO_2, hexanes, R_f = 0.42. IR(KBr) 3055, 2986 cm^{-1}. ^1H NMR($CDCl_3$, 400 MHz) δ 2.40(s, 3H), 7.24(m, 2H), 7.34

(m, 1H), 7. 45(m, 2H), 7.50(m, 2H), 7.58(m, 2H). MS(m/e) 168(M^+, base peak), 152, 77.

2-Phenylthiophene(2e): TLC, SiO_2, hexanes, $R_f = 0.52$. IR(KBr) 3070, 1608, 1477, 832, 708 cm^{-1}. ^1H NMR($CDCl_3$, 400 MHz) δ 7.09(dd, 1H, $J = 5.1$, 3.5 Hz), 7.27 (m, 2H), 7.32(dd,1H, $J = 3.5$, 1.1 Hz), 7.38(m, 2H), 7.62(m, 2H). MS(m/e) 160(M^+, base peak), 128, 115, 102, 89.

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