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Suk-Ku Kang^a, Ryung-Kee Hong^a, Tae-Hyun Kim^a & Sung-Jae Pyun^a

^a Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon, 440-746, Korea Published online: 22 Aug 2006.

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

Suk-Ku Kang,* Ryung-Kee Hong, Tae-Hyun Kim, and Sung-Jae Pyun

Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 440-746, Korea

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 products¹ and show specific properties as materials to form semiconducting charge transfer complexes² 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

^{*}To whom correspondence should be addressed.

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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 NiCl₂ 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).

$$R_1R_2I^+X^ \xrightarrow{Pd-catalyst}$$
 $R_1 - R_2$

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**

Entry	Iodonium Salts ^a	Catalyst	Zn	Draduat	solated Yield(%) ^b
1	Ph ₂ I ⁺ BF ₄ ⁻ 1a	Pd(OAc) ₂	Et ₂ Zn	Ph-Ph 2a	80
2	1a	Pd(acac) ₂	Et ₂ Zn	2a	76
3	PhI+Ph BF ₄ - 1b	Pd(OAc) ₂	Et ₂ Zn	Ph-==	rh 52 20
4	p-MeOC6H4I⁺Ph⁻OTf 1c	Pd(OAc) ₂	Et ₂ Zn	MeO- 2c Ph-Ph	46 48
5	<i>p-</i> MeC ₆ H₄I⁺Ph ⁻ OTf 1d	Pd(OAc) ₂	Et ₂ Zn		68
6	S le	Pd(OAc) ₂	Et ₂ Zn	Ze Ph	74

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

^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 MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography(hexanes, $R_t = 0.50$) to give **2a**(16.6 mg, 80%). TLC, SiO₂, hexanes, $R_t = 0.50$. IR(KBr) 3060, 1608, 1475, 831 cm⁻¹. ¹H NMR(CDCl₃, 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, SiO₂, hexanes, $R_f = 0.38$. IR(KBr) 3150, 2150, 695 cm⁻¹. ¹H NMR(CDCl₃, 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, SiO₂, hexanes, $R_f = 0.17$. IR(KBr) 3055, 1605, 1265 cm⁻¹. ¹H NMR(CDCl₃, 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, SiO₂, hexanes, $R_f = 0.42$. IR(KBr) 3055, 2986 cm⁻¹. ¹H NMR(CDCl₂, 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, SiO₂, hexanes, R_f = 0.52. IR(KBr) 3070, 1608, 1477, 832, 708 cm⁻¹. ¹H NMR(CDCl₃, 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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