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PALLADIUM-CATALYZED ARYLATION AND VINYLATION OF 2,3-DIHYDROFURAN WITH HYPERVALENT IODONIUM SALTS

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Abstract: The palladium-catalyzed arylation and vinylation of 2,3-dihydrofuran with aryl and alkenyl iodonium salts afforded 2-phenyl- or 2-alkenyl-2,5-dihydrofurans at room temperature in an aqueous medium.

Recently, the palladium-catalyzed arylation and alkenylation of 2,3dihydrofuran (1)¹ has attracted considerable interest since it offers the possibility of carrying out asymmetric coupling reactions,² as well as providing an indirect approaches to acetate and anti-aldol products.³ Usually, palladium-catalyzed arylation of 2,3-dihydrofuran affords the thermodynamically more stable 2-arylsubstituted 2,3-dihydrofurans. Larock reported^{1a-b} that palladium-catalyzed arylation and vinylation of 2,3-dihydrofuran in the presence of stoichiometric amount of silver carbonate provides the less stable 2-substituted 2,5-dihydrofurans. In connection with our projects to utilize iodonium salts in palladium-catalyzed reactions,⁴ we wish to report the palladium-catalyzed substitution of 2,3-dihydro-

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furan (1) with hypervalent iodonium salts in aqueous medium^{1g} to afford 2-substituted 2,5-dihydrofurans in the absence of silver salts at ambient temperature (Eq. 1).

$$\begin{array}{c} & & \\ & & \\ O \\ 1 \end{array} + R_1 R_2 I^+ X^- \xrightarrow{Pd(cat.)} \\ & & \\ O \\ R_1 \\ (R_2) \end{array}$$
(1)

The arylation and vinylation of 2,3-dihydrofuran with iodinanes is summarized in Table 1. The diphenyliodonium tetrafluoroborate (2a)^{5a} was coupled with the 2,3-dihydrofuran in the presence of 1,8-bis(N,N-dimethylamino) naphthalene (proton sponge) and palladium acetate (0.5 mol %) in CH₃CN/H₂O (4:1) for 10 min to afford 2-phenyl-2,5-dihydrofuran (5a) in 82% yield (entry 1 in Table 1). Using alkenyl(phenyl)iodonium tetrafluoroborate 3^{5a} under similar conditions, 2-alkenyl-substituted 2.5-dihydrofuran 6 was obtained as the sole product in 73% yield (entry 2). Coupling of p-tolyl(phenyl)iodonium tetrafluoroborate $(2b)^{5a}$ with 2,3-dihydrofuran (1) afforded 2-p-tolyl-substituted and 2-phenylsubstituted 2,5-dihydrofurans, 5b and 5a in 54% and 30% yields, respectively (entry 3). However, when triflate salt $2c^{5b}$ was used, 5b and 5a were obtained in 39% and 45% yields, respectively (entry 4). We have also coupled 2.3-dihydrofuran (1) with 2-thienvl(phenvl) iodonium tetrafluoroborate $2d^{5a}$ and tosylate 2e^{5c} to afford 2-thienyl- and 2-phenyl-substituted 2,5-dihydrofurans 5c and 5a in the ratio of 47: 30 and 49: 33, respectively (entries 5 and 6). Finally, the reaction of the iodane, μ -oxobis[(trifluoromethanesulfonato)(phenyl)iodine] (4)⁶ known as Zefirov's reagent with 2,3-dihydrofuran (1) afforded p-iodophenyl- or phenyl-substituted 2,5-dihydrofurans 5d and 5a in 57% and 43% yields, respectively (entry 7).

In summary, facile palladium-catalyzed cross-coupling of 2,3-dihydrofuran with iodinanes has been carried out at room temperature under aqueous conditions.

Entry	Iodinanes	Product ^b
1	Ph ₂ I ⁺ BF ₄ ⁻	
	2a	5a (82%)
2	$Ph \sim I^+Ph BF_4^-$	
	3	6 (73%)
3	<i>p</i> -CH ₃ C ₆ H ₄ I ⁺ Ph BF ₄ [−]	
	2ь	5b $X = Me$ 5a $X = H$ (54 : 30)
4	p-CH ₃ C ₆ H₄I⁺Ph [−] OTf 2c	5b + 5a (39:45)
5	S I ⁺ Ph BF ₄	$\overline{\langle V_0 \rangle}_{A}$
	2d	5c Y = 2-thienyl + $5a(47 : 30)$
6	S I ⁺ Ph ⁻ OTs	5c + 5a (49 : 30)
7	2e TfO- _I -O- _I -OTf Ph Ph	
	4	5d X = I 5a X = H (57 : 43)

Table 1. Palladium-Catalyzed Arylation and Vinylation of Iodinanes with2,3-Dihydrofuran (1)^a

^a All the reactions were run in CH₃CN/H₂O(4 : 1) at room temperature in the presence of proton sponge and Pd(OAc)₂(0.5 mol %) for 10 min.

^b The yields are isolated yields.

Experimental Section

Typical Procedure.

Preparation of 2-phenyl-2,5-dihydrofuran (5a)

To a stirred solution of diphenyliodonium tetrafluoroborate (0.80 g, 2.17 mmol) and proton sponge (1.40 g, 6.53 mmol) and Pd(OAc)₂ (2.5 mg, 0.5 mol %) in CH₃CN/H₂O (4 : 1) (5 mL) was added 2,3-dihydrofuran (1) (0.76 g, 10 mmol). The reaction mixture was stirred at room temperature for 10 min and quenched with saturated NH₄Cl solution (5 mL), and then extracted with ether (2 X 10 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (EtOAc/hexanes 1 : 30, Rf = 0.30) to give **5a** (0.26 g, 82%). ¹H NMR (CDCl₃, 400 MHz) δ 4.80(m, 1H), 4.88(m, 1H), 5.80(m, 1H), 5.90(m, 1H), 6.05(m, 1H), 7.29 ~ 7.38(m, 5H). IR(neat) 3028, 2964, 1612, 1598, 1472, 890 cm⁻¹. MS (m/e) 146(M⁺), 117, 115, 105(base peak), 91, 77.

2-(*p*-Tolyl)-2,5-dihydrofuran (**5b**) ¹H NMR (CDCl₃, 400 MHz) δ 2.35(s, 3H), 4.77(m, 1H), 4.86(m, 1H), 5.77(m, 1H), 5.88(m, 1H), 6.04(m, 1H), 7.15 ~ 7.21(m, 4H). IR(neat) 3034, 2932, 1621, 1601, 1481, 1372 cm⁻¹. MS (m/e) 160(M⁺), 145, 131, 119(base peak), 115, 91.

2-(2'-Thienyl)-2,5-dihydrofuran (**5c**) ¹H NMR (CDCl₃, 400 MHz) δ 4.72(m, 1H), 4.85(m, 1H), 5.94(m, 1H), 6.04(m, 1H), 6.09(m, 1H), 6.98(m, 2H), 7.27(m, 1H). IR(neat) 3098, 1594, 1400, 925, 857, 830 cm⁻¹. MS (m/e) 152(M⁺), 146, 117, 115, 105(base peak), 91, 77. 2-(*p*-Iodophenyl)-2,5-dihydrofuran (5d) ¹H NMR (CDCl₃, 400 MHz) δ 4.77(m, 1H), 4.83(m, 1H), 5.72(m, 1H), 5.84(m, 1H), 6.03(m, 1H), 7.05(m, 2H), 7.66(m, 2H). IR(neat) 3048, 2991, 1608, 1594, 1465, 884 cm⁻¹. MS (m/e) 272(M⁺), 270, 231, 145, 115(base peak), 69.

2-(2'- *trans*-Styryl)-2,5-dihydrofuran (6) ¹H NMR (CDCl₃, 400 MHz) δ 4.70(m, 1H), 4.77(m, 1H), 5.40(m, 1H), 5.82(m, 1H), 5.98(m, 1H), 6.17(dd, J = 15.8, 7.2 Hz, 1H), 6.61(d, J = 15.8 Hz, 1H), 7.24 ~ 7.40(m, 5H). IR(neat) 3054, 1640, 1610, 1455, 894, 722 cm⁻¹. MS (m/e) 172(M^{*}, base peak), 142, 129, 116, 104, 92.

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