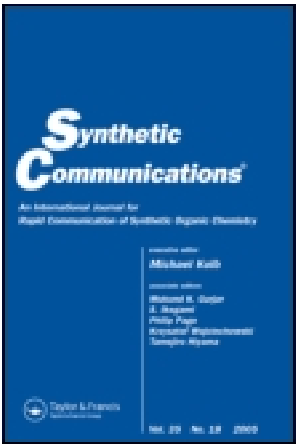

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Palladium-Catalyzed Arylation and Vinylation of 2,3-Dihydrofuran with Hypervalent Iodonium Salts

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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 2,3-dihydrofuran (**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-aryl-substituted 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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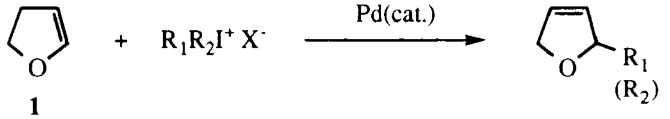
furan (**1**) with hypervalent iodonium salts in aqueous medium[1g] to afford 2-substituted 2,5-dihydrofurans in the absence of silver salts at ambient temperature (Eq. 1).

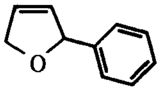
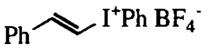
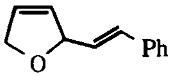
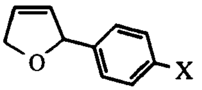
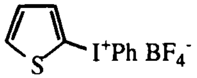
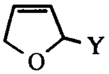
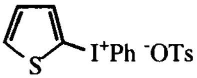
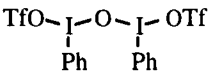
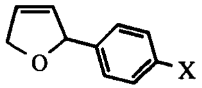


(1)

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 CH_3CN/H_2O (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-thienyl(phenyl) 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.

Table 1. Palladium-Catalyzed Arylation and Vinylation of Iodinanes with 2,3-Dihydrofuran (**1**)[a]

Entry	Iodinanes	Product[b]
1	$Ph_2I^+BF_4^-$ **2a**	 **5a** (82%)
2	 **3**	 **6** (73%)
3	*p*-$CH_3C_6H_4I^+Ph\ BF_4^-$ **2b**	 **5b** X = Me **5a** X = H (54 : 30)
4	*p*-$CH_3C_6H_4I^+Ph\ ^-OTf$ **2c**	**5b** + **5a** (39 : 45)
5	 **2d**	 **5c** Y = 2-thienyl + **5a** (47 : 30)
6	 **2e**	**5c** + **5a** (49 : 30)
7	$TfO-\underset{Ph}{I}-O-\underset{Ph}{I}-OTf$ **4**	 **5d** X = I **5a** X = H (57 : 43)

[a] All the reactions were run in $CH_3CN/H_2O(4 : 1)$ 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 CH_3CN/H_2O (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 NH_4Cl solution (5 mL), and then extracted with ether (2 X 10 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 30, Rf = 0.30) to give **5a** (0.26 g, 82%). ^1H NMR ($CDCl_3$, 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 ($CDCl_3$, 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 ($CDCl_3$, 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**) ^{1}H NMR (CDCl$_3$, 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**) ^{1}H NMR (CDCl$_3$, 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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