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Communications

Palladium-Catalyzed Carbonylation of *o*-Iodophenols with Allenes

Kazumi Okuro and Howard Alper*

Department of Chemistry, University of Ottawa,
10 Marie Curie, Ottawa, Ontario, Canada K1N 6N5

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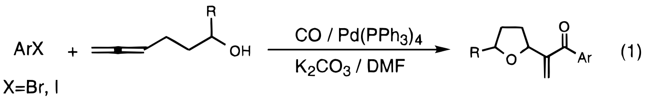
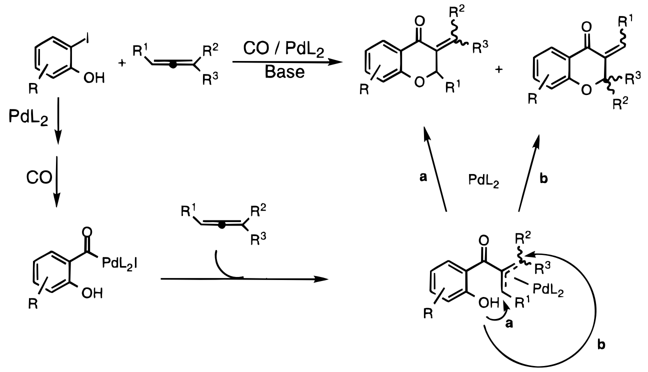
The palladium-catalyzed carbonylation of aromatic halides is one of the most versatile and convenient processes for the preparation of aromatic carbonyl compounds.[1] The reactions are considered to proceed via an aroylpalladium intermediate that is formed by oxidative addition of palladium(0) to halides, followed by insertion of carbon monoxide into the palladium−carbon bond. Although reactions using alcohols, amines, and carbon nucleophiles (including organometallic reagents) to trap aroylpalladium complexes have been well-established, much less attention has been paid to reactions with unsaturated compounds such as olefins and alkynes, in which the addition of an aroylpalladium species to a carbon−carbon multiple bond would be involved. Of particular note are the significant contributions by Negishi and co-workers on the carbonylation of aryl halides[2] bearing olefinic groups at the ortho-position and related intramolecular reactions of vinyl,[3] benzyl,[4] and allyl[5] halides. Intermolecular versions of these reactions have received less attention.[6] Recently, it has been reported that the carbonylation of aryl iodides or bromides in the presence of γ-hydroxyallenes and a palladium(0) catalyst affords aryl (tetrahydrofuran-2-yl)vinyl ketones (eq 1).[7] This reaction may occur by addition of an initially formed aroylpalladium intermediate to the allenyl unit of the γ-hydroxyallene to produce a π-allylpalladium species, which then undergoes nucleophilic attack by the hydroxyl group to give the product. We reasoned that *o*-iodophenols may undergo palladium-catalyzed carbonylative coupling with allenes, in which the attack of the phenol hydroxyl group at the π-allylpalladium intermediate would terminate the catalytic cycle affording 1-benzopyran-4-one derivatives as depicted in Scheme 1.[8] We now report the realization of this interesting reaction catalyzed by several palladium-based systems.

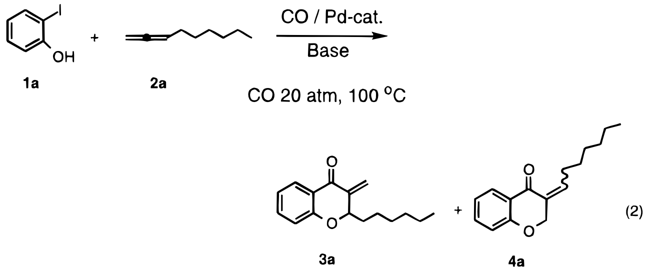


(1)

Scheme 1



Treatment of *o*-iodophenol (**1a**) (R = H) using a catalyst system containing PdCl$_2$−dppb in the presence of 1,2-nonadiene (**2a**) and (i-Pr)$_2$NEt in benzene at 100 °C for 20 h under 20 atm of carbon monoxide resulted in the formation of 2-(*n*-hexyl)-3-methylene-2,3-dihydro-4*H*-1-benzopyran-4-one (**3a**) in 63% isolated yield (eq 2). The ratio of the allene to *o*-iodophenol was 2:1, and that of allene to PdCl$_2$ and dppb was 40:1:1. The reaction gave **3a** in 27% yield in the absence of dppb. It should be noted that the reaction is regioselective; the other possible isomer, **4a**, was not detected in the reaction. The use of PPh$_3$, P(o-tolyl)$_3$, dppe, and dppp instead of dppb reduced the yield of **3a** to 33−55%. The catalyst systems Pd(OAc)$_2$−dppb and Pd$_2$(dba)$_3$·CHCl$_3$−dppb were also effective, the yield of **3a** being 73% and 68%, respectively. In addition, the reaction proceeded well using K$_2$CO$_3$ instead of the amine, affording **3a** in 74% isolated yield.



(2)

A series of allenes **2b**−**e** were reacted with *o*-iodophenols and carbon monoxide using the catalyst system Pd(OAc)$_2$−dppb, and the results are summarized in Table

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(1) (a) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (b) Coloquhom, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation*; Plenum Press: New York, 1991. (c) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: New York, 1995. (d) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

(2) (a) Negishi, E.; Tour, J. M. *Tetrahedron Lett.* **1986**, *40*, 4869. (b) Shimoyama, I.; Zhang, Y.; Wu, G.; Negishi, E. *Tetrahedron Lett.* **1990**, *31*, 2841. (c) Ma, S.; Negishi, E. *J. Org. Chem.* **1994**, *59*, 4730. (d) Negishi, E.; Coperet, C.; Ma, S.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5904.

(3) (a) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761. (b) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (c) Coperet, C.; Sugihara, T.; Wu, G.; Shimoyama, I.; Negishi, E. *J. Am. Chem. Soc.* **1995**, *117*, 3422. (d) Coperet, C.; Sugihara, T.; Negishi, E. *Tetrahedron Lett.* **1995**, *36*, 1771. (e) Negishi, E.; Ma, S.; Amanfu, J.; Coperet, C.; Miller, J. A.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5919. (f) Coperet, C.; Ma, S.; Sugihara, T.; Negishi, E. *Tetrahedron* **1996**, *52*, 11529.

(4) Wu, G.; Shimoyama, I.; Negishi, E. *J. Org. Chem.* **1991**, *56*, 6506.

(5) Negishi, E.; Wu, G.; Tour, M. *Tetrahedron Lett.* **1988**, *51*, 6745.

(6) (a) Sen, A.; Lai, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 3520. (b) Pisano, C.; Consiglio, G.; Sironi, A.; Moret, M. *J. Chem. Soc., Chem. Commun.* **1991**, 421. (c) Tanaka, H.; Abdul Hai, A. K. M.; Sadakane, M; Okumoto, H.; Torii, S. *J. Org. Chem.* **1994**, *59*, 3040. (d) Aracad, A.; Cacchi, S.; Carnicell, V.; Marinell, F. *Tetrahedron* **1994**, *50*, 437. (e) Okuro K.; Furuune, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1992**, *57*, 4754. (f) Okuro, K.; Inokawa, N.; Miura, M.; Nomura, M. *J. Chem. Res., Synop.* **1994**, 372; *J. Chem. Res., Miniprint* **1994**, 2039.

(7) (a) Walkup, R. D.; Gaun, L.; Mosher, M. D.; Kim, S. W.; Kim, Y. S. *Synlett* **1993**, 88. (b) Walkup, R. D.; Gaun, L.; Kim, Y. S.; Kim, S. W. *Tetrahedron Lett.* **1995**, *36*, 3805.

(8) Palladium-catalyzed carboannulation of functionally substituted aryl halides with 1,2-dienes and its asymmetric version have been reported; (a) Larock, R. C.; Berrios-Pena, N. G.; Fried, C. A. *J. Org. Chem.* **1991**, *56*, 2615. (b) Larock, R. C.; Zenner, J. M. *J. Org. Chem.* **1995**, *60*, 482.

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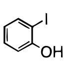
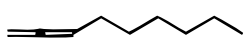
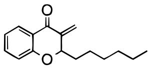
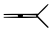
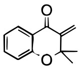
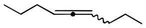
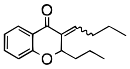
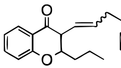
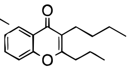
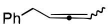
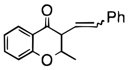
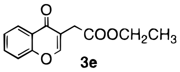
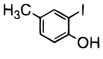
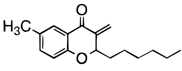
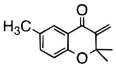
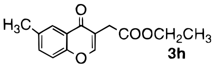
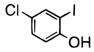
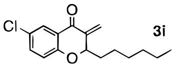
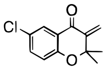
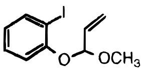
Table 1. Palladium-Catalyzed Carbonylation of *o*-Iodophenols 1 with Allenes 2^{a}

1	2	Product	Yield (%)^{b}
 **1a**	 **2a**	 **3a**	73 (74)^{c}
1a	 **2b**^{d}	 **3b**	77
1a	 **2c**	 **3c**	84^{e}
		 **3c'**  **3c''**	
1a	 **2d**	 **3d**	91
1a	 **2e**	 **3e**	29 (28)^{f}
 **1b**	**2a**	 **3f**	72
1b	**2b**^{d}	 **3g**	73
1b	**2e**	 **3h**	37
 **1c**	**2a**	 **3i**	29
1c	**2b**^{d}	 **3j**	23

^{a} Reaction conditions: [**1**]:[**2**]:[Pd(OAc)$_2$]:[dppb]:[(*i*-Pr)$_2$NEt] = 1.5:3.0:0.075:0.075:2.0 (in mmol); C_6H_6 (5.0 mL), CO 20 atm, 100 °C, 20 h. ^{b} Isolated yield is based on **1**. ^{c} Reaction using K_2CO_3 (2.0 mmol) instead of (*i*-Pr)$_2$NEt. ^{d} **2b** (6.0 mmol) was used. ^{e} **3c**: 21%. **3c′** + **3c″**: 63%. ^{f} **2e** (6.0 mmol) was used.

1. The terminal disubstituted allene, 3-methyl-1,2-butadiene (**2b**), reacted with **1a** to give the *exo*-methylene product **3b** in 77% yield. This reaction, like that of **2a**, is regioselective with nucleophilic attack of the hydroxyl group occurring exclusively at the more substituted carbon of the allene unit. When the symmetrical internal allene **2c** was employed, the expected product **3c**, its isomer **3c′**, and **3c″** were obtained in 84% combined yield. Attempts to separate **3c′** and **3c″** were unsuccessful, and consequently, their ratio could not be determined. When the unsymmetrical allene **2d** was used as the reactant, 2-methyl-3-(2-phenylvinyl)-3,4-dihydro-4*H*-1-benzopyran-4-one (**3d**) was isolated in excellent yield as the sole product. Ethyl 2,3-butadienecarboxylate (**2e**), an electron-poor allene, was less reactive than the other allenes with 3-[(ethoxycarbonyl)methyl]-4*H*-1-benzopyran-4-one (**3e**) formed in 29% yield. Furthermore, the regioselectivity was opposite to that for the alkyl-substituted allenes. It is conceivable that the initial product may contain an *exo*-methylene unit (as observed for **2a** and **2b**), which then undergoes isomerization to afford the more thermodynamically stable isomer. Reaction of **1a** with methoxyallene under standard conditions proceeded to completion, affording a complex mixture with no carbonyl-containing products. When the reaction was repeated at 60 °C, the simple adduct **5** was formed (21%) and again no carbonylation product was detected.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4-Methyl-2-iodophenol (**1b**) reacted with allenes **2a** and **2b** in an analogous manner to *o*-iodophenol, giving the expected products **3f** and **3g** in 72−73% yield, whereas the reaction of 4-chloro-2-iodophenol (**1c**) afforded the products **3i** and **3j** in 23−29% yield. The low reactivity of **1c** may be due to the modest nucleophilicity of the hydroxyl group of **1c**. Unsuccessful attempts were made to improve the yields of **3i** and **3j** by using an excess amount of (*i*-Pr)$_2$NEt (6 equiv based on **1c**) or more basic diamines such as Proton-Sponge (1,8-bis(dimethylamino)-naphthalene).[9]

In general, the present reaction is highly regioselective, in particular when terminal allenes are used, and on the basis of the results obtained the regioselectivity is apparently controlled by electronic, not steric, effects. Such trends were observed for the palladium-catalyzed heteroannulation of *o*-functionalized aryl iodides with allenes.[8]

The following general procedure was used: a mixture of **1** (1.5 mmol), **2** (3.0 mmol), Pd(OAc)$_2$ (0.075 mmol), dppb (0.075 mmol), (*i*-Pr)$_2$NEt (2.0 mmol) [or K_2CO_3 (2.0 mmol)], and benzene (5.0 mL) was reacted in an autoclave at 20 atm of carbon monoxide for 20 h at 100 °C. The reaction mixture was cooled to room temperature, diluted with ether and water, and extracted twice with ether (15 mL each time). The combined organic phase was dried over Na_2SO_4, filtered, and evaporated. The product was purified by column chromatography on silica gel using *n*-hexane−ether (95:5) as the eluant.

In conclusion, the carbonylation of *o*-iodophenols with allenes takes place in a regioselective manner, by a palladium catalyst in the presence of a base, usually affording 3-methylene-2,3-dihydro- or 3-vinyl-4*H*-1-benzopyran-4-one derivatives, often in good yields.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Council Canada for support of this research.

Supporting Information Available: General experimental procedures and characterization data for all products; ^{1}H-NMR spectra for **3a**−**j** (15 pages).

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[9] The values for the basicity of the amines (Proton-Sponge, pK_a = 12.34; aliphatic amine, pK_a ≈ 11) have been determined: Alder, R. W.; Bowman, P. S.; Steele, W. R. P.; Winterman, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 722.