Palladium-Catalyzed Hydrocarboxylation of Allenes

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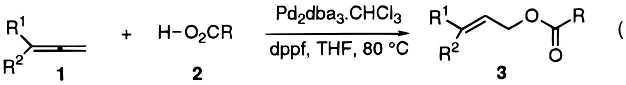
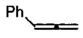
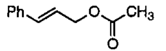
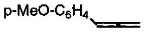
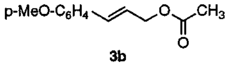
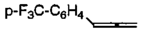
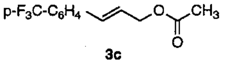
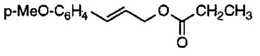
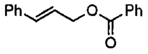
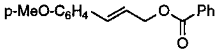
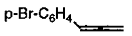
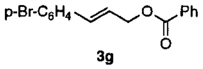
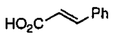
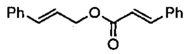
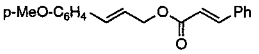
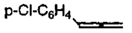
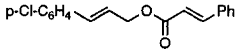
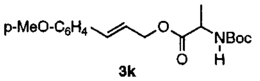
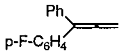
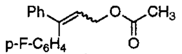
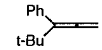
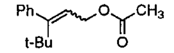
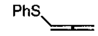
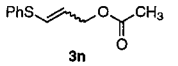
The ability of transition metal complexes to activate organic molecules makes them attractive prospects for developing catalytic processes with high selectivity and high atom economy.[1] In our continuing study on hydrocarbonation,[2] hydroamination,[3]and hydrosulfination[4] of allenes to develop a new process for eco-chemistry, we concentrated on the addition of carboxylic acids (hydrocarboxylation) to allenes. The addition of HX (X = halogen) to olefins through carbenium ions is a classical electrophilic reaction. The addition of HCl to phenylallene, which proceeds through an α-vinylbenzyl cation, has also been reported.[5] However, to the best of our knowledge, transition metal catalyzed carboxylic acid addition to allenes is not known. On the other hand, the transition metal catalyzed inter- and intramolecular addition of carboxylic acids to alkynes is well-known,[6]and the intramolecular cyclization of alkenoic acids catalyzed by palladium complexes is also known.[7]We wish to report that various types of carboxylic acids **2** smoothly react with allenes **1** in the presence of a catalytic amount (0.5−1.0 mol %) of $Pd_2(dba)_3$· $CHCl_3$/dppf complex, affording the corresponding allyl esters **3** in high chemical yields (eq 1). In contrast to the classical electrophilic addition reaction, the new version of hydrocarboxylation reaction of allenes most probably proceeds through π-allylpalladium species.



(1)

Table 1. Palladium-Catalyzed Hydrocarboxylation of Allenes[a]

Entry	Allene 1	HO_2CR 2	Product 3	Isolated yield (%)
1	 **1a**	HO_2CCH_3 **2a**	 **3a**	83
2	 **1b**	**2a**	 **3b**	81
3	 **1c**	**2a**	 **3c**	75
4	**1b**	$HO_2CCH_2CH_3$ **2b**	 **3d**	81
5	**1a**	HO2CPh **2c**	 **3e**	96
6	**1b**	**2c**	 **3f**	77
7	 **1d**	**2c**	 **3g**	71
8	**1a**	 **2d**	 **3h**	70
9	**1b**	**2d**	 **3i**	72
10	 **1e**	**2d**	 **3j**	80
11	**1b**	Boc-L-alanine **2e**	 **3k**	74
12	 **1f**	**2a**	 **3l**	96[b]
13	 **1g**	**2a**	 **3m**	74[c]
14	 **1h**	**2a**	 **3n**	86[d]

[a] All yields are of pure products isolated by column chromatography. ^1H NMR and elemental analysis either by combustion or high resolution mass spectrometry (HRMS) are satisfactory. [b] The ratio of *E*/*Z* was 50/50, determined by ^1H NMR. [c] *E*/*Z* = 75/25. [d] *E*/*Z* = 80/20.

The results are shown in Table 1. In initial experiments phenylallene **1a** was treated with 1 mol % Pd_2dba_3·$CHCl_3$ and 2 mol % dppf in THF with 1.1 equiv of acetic acid **2a**. When this reaction was carried out at room temperature, no addition product was detected. Then the reaction mixture was heated at 80 °C for 4 h. The hydrocarboxylation product, cinnamyl acetate **3a**, was isolated in 83% yield exclusively as the *E* isomer (proven by NMR spectroscopy) (entry 1). No addition product was obtained in the absence of palladium catalyst. As the catalyst, $Pd(Ph_3P)_4$/dppf was moderately effective and $[(\eta\text{-}C_3H_5)PdCl]_2$/dppf was less effective. Other catalysts such as $Pd(OAc)_2$, $PdCl_2(dppe)$, $Pt(Ph_3P)_4$, $PtCl_2(Ph_3P)_2$, K_2PtCl_4, $RhH(CO)(Ph_3P)_2$, and RuH_2-

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(1) (a) Trost, B. M. *Science* **1991**, *254*, 1471. (b) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (c) Tsuji, J. In *Palladium Reagents and Catalyst;* John Wiley & Sons: Chichester, 1995; pp 21−124.

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(3) (a) Besson, L.; Gore, J.; Cazes, B. *Tetrahedron Lett.* **1995**, *36*, 3857. (b) Al-Masum, M.; Meguro, M.; Yamamoto, Y. *Tetrahedron Lett.* **1997**, *38*, 6071 and references therein.

(4) Kamijo, S.; Al-Masum, M.; Yamamoto, Y. *Tetrahedron Lett.* **1998**, *39*, 691.

(5) (a) Okuyama, T.; Izawa, K.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 5, 6749. (b) Izawa, K.; Okuyama, T.; Sakagami, T.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 6752. (c) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110. The addition of trifluoroacetic acid to allenes was investigated. The major product was their isomerized acetylenes, and the adducts (vinyltrifluoroacetates) were obtained as a minor product.

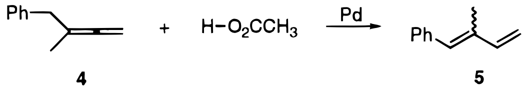
(6) (a) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 2230. (b) Chan, D. M. T.; Marder, T. B.; Milstein, D.; Taylor, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 6385. (c) Trost, B. M.; Brieden, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1335. (d) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, H. *J. Org. Chem.* **1995**, *60*, 7247 and references therein.

(7) Cyclization of alkenoic acids: Larock, R. C.; Hightower, T. R. *J. Org. Chem.* **1993**, *58*, 5298 and references therein. Two equivalents of NaOAc were used for the palladium-*catalyzed* addition of carboxylic acid to olefins and thus perhaps carboxylate RCO_2^- is formed in situ, although Prof. Larock does not mention this mechanism. Palladium would coordinate to olefin, and then the carboxylate would attack the electron-deficient olefin. Accordingly, the reaction most probably proceeds through the usual type of addition of nucleophiles to Pd(II)-coordinated alkene.

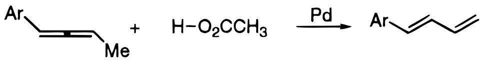
S0002-7863(97)04223-6 CCC: $15.00

$(Ph_3P)_4$ were ineffective. When $Pd_2(dba)_3{\cdot}CHCl_3$/dppf was used as the catalyst, the reactions of various allenes with various carboxylic acids were examined. When aryllallenes with an electron-donating group at the para position (e.g., *p*-MeO-C_6H_4-, **1b**) and an electron withdrawing group at the para position (e.g., *p*-F_3C-C_6H_4-, **1c**) were treated with acetic acid, the hydrocarboxylation proceeded smoothly and gave the corresponding allyl acetates **3b** and **3c**, respectively, in a regio- and stereoselective manner (entries 2 and 3). The addition of propionic acid **2b** to **1b** proceeded satisfactorily (entry 4). With benzoic acid **2c**, the addition to allene **1a**, **1b**, and *p*-bromophenylallene **1d** gave the corresponding allyl esters **3e**, **3f,** and **3g**, respectively, in very high yields (entries 5−7). The hydrocarboxylation of **1a**, **1b**, and *p*-chlorophenylallene **1e** with cinnamic acid **2d** proceeded very smoothly, giving the corresponding carboxylates **3h**, **3i**, and **3j**, respectively, in good yields (entries 8−10). When *p*-methoxyphenylallene was treated with Boc-L-alanine **2e**, the corresponding allyl ester of Boc-L-alanine **3k** was obtained in good yield without affecting the functional groups (entry 11). α,α-Disubstituted allenes, **1f** and **1g**, reacted very smoothly with **2a** to give the corresponding allylic carboxylates **3l** and **3m**, respectively, in good to high yields (entries 12−13). Very interestingly, phenylthioallene **1h** underwent the hydrocarboxylation reaction without any problem to afford the acetoxylate **3n** having a vinylthio group in high yield (entry 14).

In the case of aliphatic allenes, 1,3-butadiene type products were formed;[8] the reaction of a 1,1-disubstituted allene **4** with acetic acid gave an isomerized 1,3-butadiene **5** (*E*: *Z* = 1:1) in 50% yield (eq 2). Furthermore, α-aryl- and γ-methyl-substituted allenes **6a**,**b**,**c**, gave 1-aryl-1,3-butadienes in ca. 50% yields upon treatment with acetic acid−Pd catalyst (eq 3). Accordingly, if there is an allylic hydrogen in aliphatic allenes, β-hydride elimination from the π-allylpalladium intermediate **8** (*vide post*) predominates over reductive coupling, giving the diene derivatives as a major product.



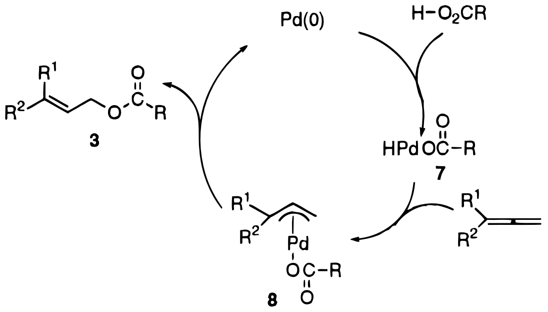
(2)



(3)

6a, Ar = *p*-F_3C-C_6H_4
6b, Ar = *p*-F-C_6H_4
6c, Ar = Ph

Scheme 1



A typical procedure is as follows. To a dry reaction vial (the Wheaton microreactors), charged with $Pd_2dba_3{\cdot}CHCl_3$ (0.005 mmol, 5.5 mg), dppf (0.01 mmol, 6.0 mg), and THF (0.5 mL), were added acetic acid (0.55 mmol, 0.04 mL) and phenylallene **1a** (0.5 mmol, 0.068 mL), and the reaction mixture was heated at 80 °C for 4 h. The mixture was filtered through a short alumina column. Removal of the solvent in vacuo followed by silica gel column chromatography with hexane/ethyl acetate (60/1) as an eluent provided pure cinnamyl acetate in 83% yield (73.0 mg). Various allenes were prepared by the reaction of aryl (or alkyl) copper reagents with propargyl tosylates.[9] Phenylthioallene was prepared from phenylthiocopper complex with propargyl chloride.[10]

A plausible mechanism for the new catalytic reaction is shown in Scheme 1. Insertion of Pd(0) would produce hydridopalladium species **7**. Hydropalladation of an allene with **7** would give a π-allylpalladium intermediate **8**, which would afford allylcarboxylate **3** and Pd(0) via reductive elimination.

A remarkable feature of the present reaction is its efficiency, especially the high yields of hydrocarboxylated products under mild conditions with excellent regio- and stereoselectivity (in the case of the monosubstituted allenes). A new version of $H{-}O_2CR$ addition to allenes most probably involves hydridopalladium species followed by π-allyl complex, instead of a carbenium ion intermediate in classical electrophilic addition. The molar ratio of reactant/catalyst is high enough for a synthetic reaction and the catalytic process described here may be useful for synthesizing a new range of allylated esters.

Supporting Information Available: Full spectroscopic and analytical characterization of the products (17 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[8] (a) Tsuji, J. In *Adv. Org. Chem.* **1979**, *17*, 141−193. (b) Shimizu, I.; Sugiura, I.; Tsuji, J. *J. Org. Chem.* **1985**, *50*, 537.

[9] Vermer, P.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 112.

[10] Bridges, A. J. *Tetrahedron Lett.* **1980**, *21*, 4401.