Pd(0)–PhCOOH catalyzed addition of oxygen pronucleophiles to allenes and internal alkynes[1]

Nitin T. Patil, Nirmal K. Pahadi, and Yoshinori Yamamoto

Abstract: We have developed a catalytic system that enables the addition of alcohols to allenes using a combination of 5 mol% $Pd(PPh_3)_4$ and 10 mol% benzoic acid. Likewise, the addition reaction of carboxylic acids to alkynes is described. In all cases the reaction proceeded well, giving the corresponding allylation products in good-to-high yields with high regio- and stereoselectivities.

Key words: addition, alcohols, carboxylic acids, allenes, alkynes, palladium.

Résumé : Nous avons développé un système catalytique qui utilise une combinaison de 5 mol% de $Pd(PPh_3)_4$ et de 10 mol% d'acide benzoïque et qui permet de réaliser l'addition d'alcools à des allènes. On décrit aussi la réaction d'addition d'acides carboxyliques à des alcynes. Dans tous les cas, la réaction se produit bien et conduit aux produits d'allylation correspondants avec des rendements allant de bons à élevés et avec des régio- et stéréosélectivités élevées.

Mots clés : addition, alcools, acides carboxyliques, allènes, alcynes, palladium.

[Traduit par la Rédaction]

Introduction

Transition metal catalyzed addition of nucleophiles to activated C—C bonds is one of the most important processes in organic synthesis. The addition of carbon pronucleophiles to activated C—C bonds is commonly referred to as a hydrocarbonation (1) reaction. Likewise, the addition reactions of amines and alcohols across an activated C—C bond are referred to as hydroamination (2) and hydroalkoxylation (3), respectively. All these processes are very important from the synthetic point of view because, in principle, the addition reactions can be performed with 100% atom efficiency, without any waste formation, and for this reason they fulfill the requirements of green chemistry, in contrast to substitution reactions. Although tremendous amounts of related work have been carried out in the field of hydrocarbonation and hydroamination reactions, very few reports have been found for the hydroalkoxylation and hydrocarboxylation reactions, partly because of the diminished nucleophilicity and the softer Lewis base character of oxygen nucleophiles as compared with amines.

Our interest in these type of addition reactions has prompted us to investigate a catalytic system for the addition of carbon and nitrogen pronucleophiles to allenes (2*a*, 4). As part of our ongoing interest in this area, we extended this approach to the intermolecular addition of carboxylic acids (5) to allenes (eq. [1]). In the latter case, it was found that the reaction was completed in a shorter time period (4 h), giving the allylation products in high yields with high stereo- and regioselectivity, in contrast to the previously reported cases (4) wherein the addition of carbon nucleophiles proceeded but the products were obtained in lower yields and consisted of a mixture of *E* and *Z* stereoisomers. This difference in reaction pathways in the case of carboxylic acid pronucleophiles and carbon pronucleophiles prompted us to study the catalytic system closely. To our delight, we found that, in this palladium catalyzed reaction, the addition of a catalytic amount of carboxylic acid is crucial for obtaining the allylation products in high yields and in a regio- and stereoselective manner. Our unique finding (Pd(0)–RCOOH combined catalyst) has also been successfully applied to the addition of nitrogen (6) and carbon (7) nucleophiles. However, the addition of alcohols to allenes under the newly developed procedure remains to be disclosed.

The addition of various pronucleophiles to alkynes is also a subject of interest in our laboratory (8). We recently reported a new approach for the allylation of carbon (8*a*–8*d*) and nitrogen (8*d*–8*g*) pronucleophiles with alkynes in the presence of a Pd(0)–carboxylic acid combined catalyst. Later we communicated the formal addition of alcohol to alkynes (eq. [2]) (8*h*). However, the addition of carboxylic acid to alkynes has not been addressed until now by our group. In the meantime, Zhang et al. (9) reported the addition of oxygen nucleophiles to alkynes using the catalytic system developed by us without citing our (8*h*) reference. In this paper we report, in detail, our efforts in the successful implementation of our newly developed Pd(0)–PhCOOH combined catalyst system for the addition of alcohols to

Received 17 November 2004. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 2 June 2005.

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[1]This article is part of a Special Issue dedicated to Professor Howard Alper.
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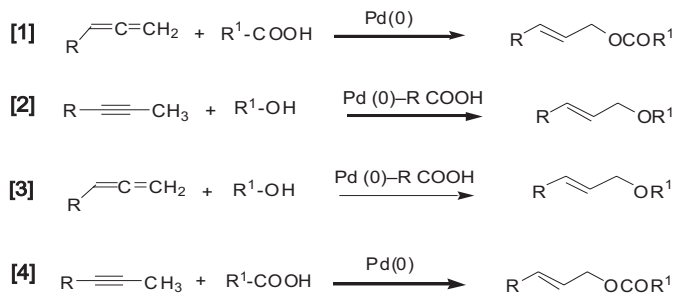
 doi: 10.1139/V05-043

allenes (eq. [3]) and the addition of carboxylic acids to alkynes in a regio- and stereoselective manner (eq. [4]).



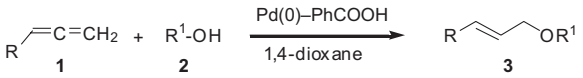
Results and discussion

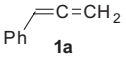
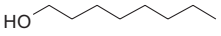
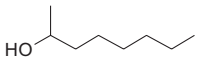
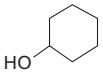
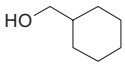
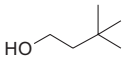
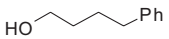
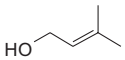
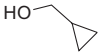
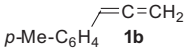
Heating a mixture of phenyl allene **1a** and acetic acid in the presence of Pd_2dba_3·$CHCl_3$ and dppf in THF at 80 °C for 4 h under argon resulted in the formation of cinnamyl acetate in 83% yield, with excellent regio- and stereoselectivity (eq. [1], R = Ph, R^1 = CH_3) (5). However, when phenyl allene was treated with carbon pronucleophiles (for instance, methylmalononitrile) under similar conditions, the reaction time was increased to 48 h (4*a*). Moreover, in most cases, the products were obtained in lower yields and consisted of a mixture of *E* and *Z* stereoisomers. At this stage the exact reason behind the superiority of the addition of carboxylic acid pronucleophiles to allenes over carbon pronucleophiles was not known. After detailed investigation into the reaction, we found that the combination of Pd(0) and carboxylic acid was best (see mechanistic part mentioned later). A dramatic change was observed when a catalytic amount of a carboxylic acid was introduced into the reaction system. The discovery of the unique role of a carboxylic acid as an additive allowed us to perform the addition of nitrogen (6) and carbon (7) nucleophiles to allenes in a highly stereo- and regioselective manner and in a shorter time. As a part of our continuing interest in this area, we then decided to study the intermolecular addition of alcohols to allenes. The results are summarized in Table 1.

Treatment of phenyl allene **1a** with benzyl alcohol **2a** under standard conditions gave the corresponding allylation product **3a** in 71% yield (entry 1). Likewise, in the hydrocarbonation (7) and hydroamination (6) of allenes, the reaction of phenyl allene **1a** with various alcohols proceeded smoothly to afford the products **3b**–**3j** in good yields (entries 2–10). Substituents such as -CH_3 and -F in the aromatic nucleus of allenes do not affect the efficiency of the reaction. Thus, when **1b** and **1c** were treated with benzyl alcohol, the corresponding allylation products **3k** and **3l** were obtained in 68% and 72% yield, respectively (entries 11 and 12).

Next, we turned our attention towards the addition of carboxylic acids to alkynes. A mixture of 1-phenyl-1-propyne (**4a**) and acetic acid (1.5 equiv.) in the presence of $Pd(PPh_3)_4$ (5 mol%) was heated in 1,4-dioxane at 100 °C for 12 h. As anticipated, the starting materials were completely consumed, giving the allylation product **6a** in 81% isolated yield as a single stereoisomer (Table 2, entry 1) (8*a*). Other acids such as 2-furoic acid (**5b**), hexanoic acid (**5c**), 1-naphthoic acid (**5d**), and 2,2-diphenylacetic acid (**5e**) reacted

Table 1. Addition of alcohols to allenes.



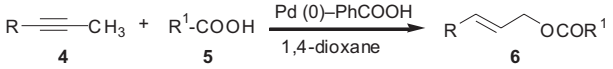
Entry	Allene (**1**)	Alcohol (**2**)	Product (**3**)	Yield (%)[a]
1	 **1a**	BnOH	**3a**	71
2	**1a**		**3b**	70
3	**1a**		**3c**	75
4	**1a**		**3d**	71
5	**1a**		**3e**	75
6	**1a**		**3f**	79
7	**1a**		**3g**	70
8	**1a**		**3h**	75
9	**1a**		**3i**	65
10	**1a**		**3j**	75
11	 **1b**	BnOH	**3k**	68
12	 **1c**	BnOH	**3l**	72

Note: All reactions were carried out as per the general procedure described in the Experimental section.
[a]Isolated yields.

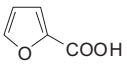
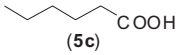
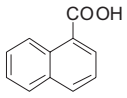
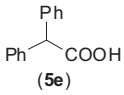
well with alkyne **4a**, giving the corresponding allylation products in high yields (entries 2–5). The aryl alkynes bearing -OMe and -Cl substituents at the *para* position, **4b** and **4c**, reacted well with **5e** and **5c** to give the products **6f** and **6g**, respectively, in excellent yields (entries 6 and 7).

The mechanism of this reaction is presumably similar to those reported previously (8) and is shown in Fig 1. The initial step is the hydropalladation of alkynes **4** with the hydridopalladium species **8** generated from Pd(0) and benzoic acid (catalytic cycle I). The resulting vinyl palladium species **7** would produce phenyl allene **1** and the active catalyst **8** via β-elimination. Hydropalladation of **1** with **8** presumably gives the π-allylpalladium species **9**, which reacts with alcohols and carboxylic acids to give allylation products, along with the hydridopalladium species **8** (cycle II). In

Table 2. Addition of carboxylic acids to alkynes.



4 5 6

Entry	Alkyne (**4**)	R^1COOH(**5**)	Product (**6**)	Yield (%)[a]
1	**4a** R = C_6H_5	CH_3COOH (**5a**)	**6a**	81
2	**4a**	 (**5b**)	**6b**	75
3	**4a**	 (**5c**)	**6c**	90
4	**4a**	 (**5d**)	**6d**	90
5	**4a**	 (**5e**)	**6e**	83
6	**4b** R = C_6H_4-*p*-OMe	**5e**	**6f**	95
7	**4c** R = C_6H_4-*p*-Cl	**5c**	**6g**	90

Note: All reactions were carried out as per the general procedure described in the Experimental section.

[a]Isolated yields.

short, in the case of alkynes both cycles I and II operate, while in the case of allenes only cycle II operates.

In conclusion, the Pd(0)–benzoic acid catalyzed allylation of alcohols and carboxylic acids with allenes and alkynes provides a new route to allyl ethers and allyl carboxylates, respectively. Although we proposed that a role of the carboxylic acid in this catalytic system would be the formation of the hydridopalladium species (8), the precise nature and a more detailed investigation on the catalytic species should be carried out in future (10).

Experimental section

General procedure for the addition of oxygen pronucleophiles to allenes–alkynes

To a mixture of phenyl allene – 1-phenyl-1-propyne (0.4304 mmol), alcohols – carboxylic acids (0.6456 mmol), and tetrakis(triphenylphosphine)palladium (0.022 mmol) in dry 1,4-dioxane (2 mL) was added acetic acid (0.043 mmol), and the mixture was stirred at 100 °C for 12 h in a screw-capped vial. The reaction mixture was then filtered through a short silica gel column using ether as an eluent, and the filtrate was concentrated. The residue was purified by recycling preparative HPLC (LC-918), using chloroform as an eluent to give the allylated products. Structures of **3a**–**3e** (8*h*), **3g** and **3h** (8*h*), **3j** (8*h*), **6a** (9), and **6b** (11) are known in the literature. The characterization data for the newly synthesized compounds **3f**, **3i**, **3k**, **3l**, and **6c**–**6g** are given below.

3f

IR (neat) (cm^{-1}): 1615. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.20 (m, 5H), 6.60 (d, *J* = 16.1 Hz, 1H), 6.30 (dt, *J* = 16.1, 6.1 Hz, 1H), 4.13 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.55 (t, *J* = 7.6 Hz, 2H), 1.58 (t, *J* = 7.6 Hz, 2H), 0.92 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.6, 131.9, 128.4, 127.5, 126.4, 71.5, 67.8, 43.1, 29.8, 29.7. HR-MS calcd. for $C_{15}H_{22}O$ ($[M]^+$): 218.1671; found: 218.1665.

3i

IR (neat) (cm^{-1}): 1622. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.21 (m, 5H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.01 Hz, 1H), 4.16 (dd, *J* = 6.01, 1.4 Hz, 2H), 3.33 (d, *J* = 6.8 Hz, 2H), 1.16–1.06 (m, 1H), 0.62–0.51 (m, 2H), 0.26–0.22 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.7, 132.2, 128.4, 127.5, 126.4, 126.3, 75.1, 71.2, 10.8. HR-MS calcd. for $C_{13}H_{16}O$ ($[M]^+$): 188.1201; found: 188.1196.

3k

IR (neat) (cm^{-1}): 1606. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.35–7.01 (m, 9H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.1 Hz, 1H), 4.5 (s, 2H), 4.15 (dd, *J* = 6.1, 1.2 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.2, 137.4, 133.8, 132.5, 129.2, 128.3, 127.7, 127.5, 126.3, 124.9, 72.0, 70.9, 21.3. HR-MS calcd. for $C_{17}H_{18}O$ ($[M]^+$): 238.1358; found: 238.1352.

3l

IR (neat) (cm^{-1}): 1606. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.29–7.21 (m, 7H), 6.92 (t, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.11 (dt, *J* = 16.1, 5.9 Hz, 1H), 4.50 (s, 2H), 4.10 (dd, *J* = 5.9, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.5, 138.1, 132.8, 131.2, 128.4, 127.9, 127.9, 127.7, 127.6, 125.7, 115.5, 72.3, 70.7. HR-MS calcd. for $C_{16}H_{15}FO$ ($[M]^+$): 242.1107; found: 242.1101.

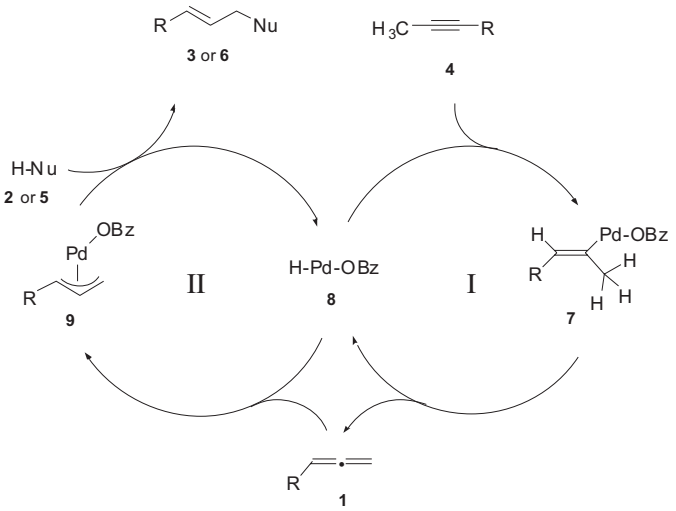
6c

IR (neat) (cm^{-1}): 1735, 1598. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.35–7.11 (m, 5H), 6.56 (d, *J* = 15. 9 Hz, 1H), 6.20 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.65 (dd, *J* = 6.3, 2.0 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.62–1.51 (m, 2H), 1.28–1.19 (m, 4H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 173.5, 136.2, 133.9, 128.5, 127.9, 126.5, 123.3, 64.8, 34.3, 31.4, 24.7, 22.4, 13.9. HR-MS calcd. for $C_{15}H_{20}O_2$ ([M + Na]): 255.1355; found: 255.1356.

6d

IR (neat) (cm^{-1}): 1708, 1620. ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.51 (s, 1H), 7.96 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.32 Hz, 2H), 7.43–7.06 (m, 7H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.30 (dt, *J* = 15.7, 6.3 Hz, 1H), 4.88 (dd, *J* = 6.3, 1.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.3, 136.1, 135.4, 134.2, 132.3, 130.9, 129.2, 128.6, 128.5, 128.3, 128.1, 127.9, 127.6, 127.3, 126.5, 126.4, 125.1, 123.2, 65.6. HR-MS calcd. for $C_{20}H_{16}O_2$ ([M + Na]): 311.1045; found: 311.1043.

Fig. 1. A mechanism for the addition of *O*-nucleophiles to allenes and alkynes.



6e

IR (neat) (cm^{-1}): 1732, 1598. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.27–7.15 (m, 15H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.17 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.50 (s, 1H), 4.72 (dd, *J* = 6.3, 1.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 172.1, 138.5, 136.1, 134.1, 128.6, 128.5, 128.4, 127.9, 127.2, 126.5, 122.8, 65.6, 57.1. HR-MS calcd. for $C_{23}H_{20}O_2$ ([M + Na]): 351.1354; found: 351.1356.

6f

IR (neat) (cm^{-1}): 1732, 1606. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.24–7.12 (m, 12 H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.00 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.96 (s, 1H), 4.66 (dd, *J* = 6.6, 1.0 Hz, 2H), 3.64 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 172.1, 159.4, 138.5, 133.9, 128.8, 128.5, 128.4, 127.7, 127.1, 120.4, 113.9, 65.9, 57.0, 55.2. HR-MS calcd. for $C_{24}H_{22}O_3$ ([M + Na]): 381.1569; found: 381.1584.

6g

IR (neat) (cm^{-1}): 1735, 1633. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.32–7.25 (m, 4H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.72 (dd, *J* = 6.3, 1.2 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.69–1.56 (m, 2H), 1.36–1.27 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 173.4, 134.7, 133.6, 132.6, 128.7, 127.7, 124.0, 64.6, 34.3, 31.4, 24.7, 22.4, 13.9. HR-MS calcd. for $C_{15}H_{19}ClO_2$ ([M + O + Na]): 305.0914; found: 305.0915.

Acknowledgements

N.T.P. thanks the Japan Society for the Promotion of Science (JSPS) for a postdoctoral research fellowship.

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