

Synthetic Methods

CO/C-H as an Acylating Reagent: A Palladium-Catalyzed Aerobic Oxidative Carbonylative Esterification of Alcohols**

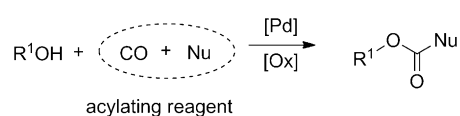
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Abstract: A palladium-catalyzed oxidative carbonylative esterification of a variety of functionalized alcohols under base- and ligand-free conditions has been demonstrated. A CO/olefin combination was utilized as the acylating reagent with O_2 as a benign oxidant. Notably, the scope of the substrate alcohols has been greatly broadened.

Esterification is a fundamental transformation in both academic research and industrial chemistry as esters are among the most important functional groups and are found widely in fine chemicals, natural products, and polymers.^[1] Traditionally, esters are prepared by the reaction of alcohols with activated acid derivatives such as acyl halides.^[2] However, the corrosive and unstable properties of acyl halides and the generation of unwanted byproducts make this process far from satisfactory.

In recent years, transition-metal catalysis has emerged as a powerful tool for promoting the esterification of alcohols. Several new type of acylating reagents, such as aldehydes,^[3] have been used for the esterification of alcohols under transition-metal catalysis. In the meantime, carbonylation has recently been utilized to introduce a synthetically versatile carbonyl group to various organic molecules in a very efficient manner.^[4] In this case, the CO/RX (organo electrophiles) system was used as the acylating reagent for esterifying alcohols through carbonylative esterification.^[5] As a result, the electrophiles (RX) are mainly obtained from the pre-functionalization of the corresponding C-H compounds, and more and more attention has been paid to the direct oxidative R-H carbonylation process, in which CO/RH are utilized as the acylating reagents on account of the high atom and step economy.^[4a-c,6] O_2 is considered an ideal terminal oxidant in oxidative transformations and several reports have been demonstrated in oxidative carbonylative esterification of

alcohols with O_2 as the terminal oxidant.^[7] In almost all of those reactions, the attention was mainly focused on the generality of R-H reagents. Actually, from the point view of the alcohol, CO/RH could be considered an ideal acylating reagent for alcohol esterification. However, to the best of our knowledge, of the reported oxidative carbonylative esterifications, alcohols were all utilized as the sacrificial reagents in excess to enhance the reaction efficiency.^[6e,7a,8] In many cases, alcohols need to be used as the solvents. The main issue might be related to the easy oxidation of alcohols under the reaction conditions. Thus, substrate applicability of different kinds of alcohols is greatly restricted. Herein, we demonstrate a palladium-catalyzed aerobic oxidative carbonylative esterification of alcohols to directly construct α,β -unsaturated esters under base- and ligand-free conditions, wherein a CO/olefinic system was utilized as the acylating reagent (Scheme 1). Importantly, only stoichiometric amounts of the alcohol are required, and the use of structurally complex alcohols is allowed in this oxidative carbonylative esterification for the synthesis of α,β -unsaturated esters.



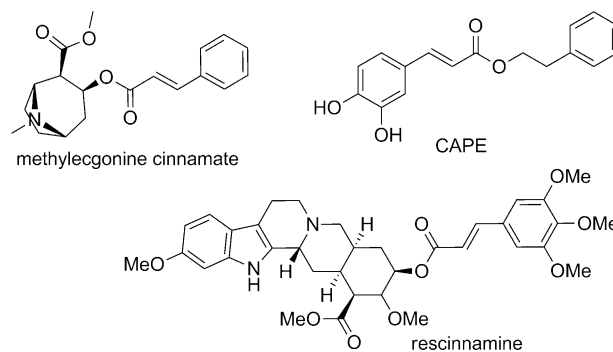
Scheme 1. Palladium-catalyzed oxidative carbonylative esterification of alcohols.

α,β -Unsaturated esters are important chemical feedstocks and they not only exist in numerous biologically active molecules and natural products (Scheme 2),^[9] but also serve as useful synthetic intermediates in organic synthesis.^[10] Therefore, there is a demand for developing a sustainable

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[**] This work was supported by the 973 Program (2011CB808600), the National Natural Science Foundation of China (21390400, 21025206, 21272180 and 21302148), and the Research Fund for the Doctoral Program of Higher Education of China (20120141130002).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201400612>.



Scheme 2. Selected examples of significant α,β -unsaturated esters containing pharmaceuticals and natural products.

and atom-economic method for the synthesis of α,β -unsaturated esters.

We started our experiments by using benzyl alcohol (**1a**) and 4-methylphenylene (**2a**) as the substrates in a ratio of 1:1. After considerable effort, we found that a cosolvent system of toluene and DMSO was appropriate. In the presence of PdCl₂ (3 mol %), and Cu(OAc)₂·H₂O (20 mol %) under an atmosphere of CO/O₂ (1:7) at 80 °C for 14 hours, the desired product **3aa** was obtained in 80 % yield (Table 1, entry 1).

Table 1: Impact of reaction parameters on the efficiency of palladium catalyzed oxidative carbonylation of **1a** with **2a**.^[a]

$\text{Ph-CH}_2\text{OH} + \text{CO} + \text{CH}_2=\text{CH-C}_6\text{H}_4\text{Me} \xrightarrow[\text{O}_2, 80^\circ\text{C}, 14\text{ h}]{\text{[Pd] (3 mol\%), [Cu] (20 mol\%)}, \text{toluene/DMSO}} \text{Ph-CH}_2\text{O-CO-CH=CH-C}_6\text{H}_4\text{Me}$			
Entry	[Pd]	[Cu]	Yield [%] ^[b]
1	PdCl ₂	Cu(OAc) ₂ ·H ₂ O	80
2 ^[c]	PdCl ₂	Cu(OAc) ₂ ·H ₂ O	88 (85)
3	Pd(OAc) ₂	Cu(OAc) ₂ ·H ₂ O	76
4	[PdCl ₂ (PPh ₃) ₂]	Cu(OAc) ₂ ·H ₂ O	71
5	PdCl ₂	—	n.d.
6	PdCl ₂	CuCl ₂	n.d.
7	PdCl ₂	CuBr ₂	n.d.
8 ^[d]	PdCl ₂	Cu(OAc) ₂ ·H ₂ O	52

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), palladium salts (0.015 mmol) and copper salts (0.1 mmol), CO/O₂ = 1:7 (1 atm), toluene/DMSO = 1.0 mL:0.1 mL, 80 °C, 14 h. [b] The yield was determined by GC analysis and calibrated using biphenyl as the internal standard. [c] 20 h. The yield within parentheses is that of the isolated product. [d] Toluene/DMF = 1:0.1 mL. DMSO = dimethylsulfoxide, n.d. = not detected.

Prolonging the reaction time to 20 hours resulted in an increased yield of 88% (85% upon isolation; Table 1, entry 2). The yield of the desired product **3aa** was decreased slightly when PdCl₂ was replaced by either [PdCl₂(PPh₃)₂] or Pd(OAc)₂ (Table 1, entries 3 and 4). Product was not obtained in the absence of Cu(OAc)₂·H₂O (Table 1, entry 5). Replacing of Cu(OAc)₂·H₂O with CuCl₂ or CuBr₂ delivered no desired product (Table 1, entries 6 and 7). The variation of the mixed solvent to toluene/DMF also led to reduced efficiency in terms of chemical yield (Table 1, entry 8). Notably, when toluene was employed as the sole solvent, only 5% yield of the desired product **3aa** was obtained, and no benzaldehyde was detected (see Figure 1 a in the Supporting Information). When toluene was replaced by DMSO, the yield of the desired product increased to 11%, and the amount of alcohol oxidation increased greatly to a 57% yield (see Figure 1 b in the Supporting Information). These results highlighted the significance of the cosolvent system.

Next, the substrate scope of various alcohols with **2a** was explored. Delightfully, the results in Table 2 demonstrated a high degree of functional-group tolerance for the alcohols. A series of α,β -unsaturated esters were obtained in good to excellent yields. Various substituted aryl methanols bearing electron-withdrawing groups, such as 4-NO₂ (**3ca**), and electron-donating groups, such as 4-OMe (**3ba**), were well tolerated, thus giving the desired products in good yields. 3,5-

Table 2: Palladium-catalyzed oxidative carbonylative esterification of various alcohols **1** with **2a**.^[a]

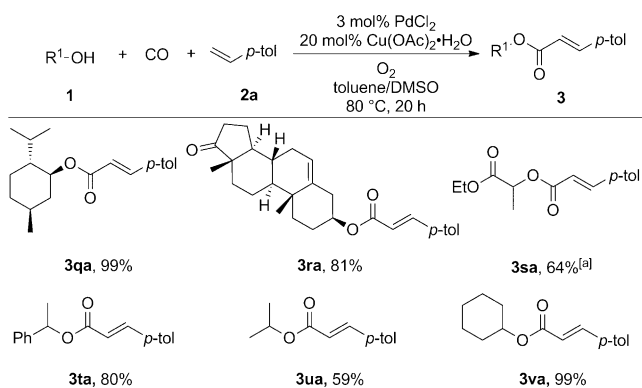
$\text{R}^1\text{OH} + \text{CO} + \text{CH}_2=\text{CH-C}_6\text{H}_4\text{Me} \xrightarrow[\text{toluene/DMSO}, 80^\circ\text{C}, 20\text{ h}]{\text{3 mol\% PdCl}_2, \text{20 mol\% Cu(OAc)}_2\cdot\text{H}_2\text{O}, \text{O}_2} \text{R}^1\text{O-CO-CH=CH-C}_6\text{H}_4\text{Me}$				
Entry	1		3	Yield [%] ^[b]
1		R = OMe (1b)	3ba	81
2		R = NO ₂ (1c)	3ca	69
3		R = F (1d)	3da	97
4		(1e)	3ea	83
5		(1f)	3fa	85
6		(1g)	3ga	98
7		(1h)	3ha	66
8		(1i)	3ia	91
9		(1j)	3ja	94
10		(1k)	3ka	64
11		(1l)	3la	57
12		(1m)	3ma	80
13		(1n)	3na	79
14		(1o)	3oa	50
15 ^[c]		(1p)	3pa	89

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), PdCl₂ (0.015 mmol), Cu(OAc)₂·H₂O (0.1 mmol), CO/O₂ = 1:7 (1 atm), in toluene (1 mL) and DMSO (0.1 mL) at 80 °C for 20 h. [b] Yield of isolated product. [c] 1.0 mmol **2a** was applied.

Dimethoxyphenylmethanol also proceeded to afford the desired product **3ea** (83%). Aryl methanols substituted with halogens, such as F and Cl, could also be acylated to generate the desired products in excellent yields (**3da** and **3fa**). Other aromatic substrates such as the naphthyl **3ga** and furyl **3ha** were well tolerated.

Notably, a variety of primary aliphatic alcohols were tested and proved to be perfect coupling partners in this oxidative carbonylative esterification, thus giving the corresponding products in good to excellent yields (Table 2, entries 8–12). In addition, different kinds of functional groups such as chloro (**3ja**), carbonyl (**3la**), and even acetal groups (**3ma**) were tolerated in this transformation. Allylic alcohol derivatives also showed good reaction efficiency, thus generating the target products in moderate to good yields (Table 2, entries 13 and 14). For diol compounds such as 2,2-dimethylpropane-1,3-diol, both of the hydroxy groups participated in the oxidative carbonylative esterification to afford the corresponding diester **3pa** in good yield (Table 2, entry 15). In the cases shown in entries 10, 11, and 14 of Table 2, the relatively low yields are due to the incomplete conversion of the starting materials, and might result from the catalyst decay as palladium black was also observed.

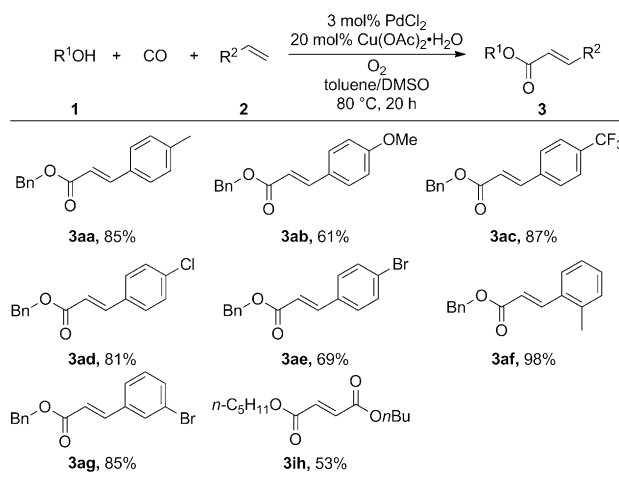
To further explore the applicability of alcohols, various secondary alcohols were also investigated (Scheme 3). L-Menthol and dehydroepiandrosterone (DHEA), which widely exist in plants and animals, reacted smoothly with **2a** to provide the corresponding oxidative carbonylation products in good to excellent yields (**3qa** and **3ra**). Ethyl lactate was also compatible, and the desired product **3sa** was obtained in 64% yield. The reaction of **2a** with simple benzylic and aliphatic secondary alcohols, such as 1-phenylethanol, isopropanol, and cyclohexanol also proceeded to afford the desired α,β -unsaturated esters in good to excellent yields (**3ta**, **3ua**, and **3va**).



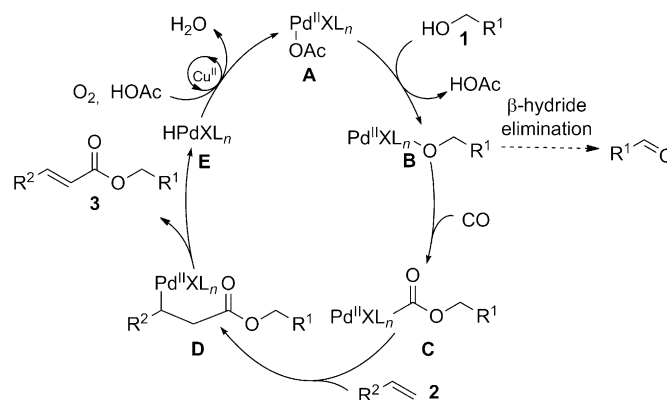
Scheme 3. Palladium-catalyzed oxidative carbonylation reactions of various secondary alcohols with **2a**. Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), PdCl₂ (0.015 mmol), Cu(OAc)₂·H₂O (0.1 mmol), CO/O₂ = 1:7 (1 atm), in toluene and DMSO (1:0.1) at 80 °C for 20 h. Yield is that of the isolated product. [a] 38 h.

Subsequently, we investigated the applicability of various alkenes in this transformation, and the results are listed in Scheme 4. Both electron-donating and electron-withdrawing substituents on styrene were well-tolerated in this reaction (**3ab** and **3ac**). Styrenes with alkyl substituents, such as methyl, afforded the desired product in good to excellent yields (**3aa**, **3af**). Notably, chloro or bromo substituents (*p*-Cl, *p*-Br, and *m*-Br) were well tolerated and the corresponding esters **3ad**, **3ae**, and **3ag** were obtained in good yields. The halide functionalities provide the possibility for further functionalization on the phenyl ring of styrene. Furthermore, butyl acrylate readily reacted with pentan-1-ol to get the desired fumaric ester in 53% yield (**3ih**). The relatively low yield is due to the incomplete conversion of the starting materials.

This transformation is believed to proceed by the catalytic cycle shown in Scheme 5.^[6e,8,11] Initially, an alkoxy palladium intermediate **B** is generated from the reaction between **1** and the Pd^{II} species **A** through an alcoholysis step. As the reaction proceeds in the absence of base, the acetate ligand is believed to promote this alcoholysis and HOAc is generated.^[12] Then, **B** undergoes CO insertion to generate **C** and then olefin insertion generates the intermediate **D**. β -Hydride elimination of **D** affords the final product **3** and releases a palladium hydride species **E** which is oxidized by O₂ and the copper catalyst in the presence of HOAc to regenerate Pd^{II} and



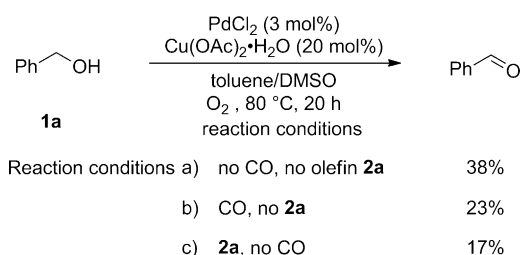
Scheme 4. Palladium-catalyzed oxidative carbonylation reactions of various alkenes with alcohols. Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), PdCl₂ (0.015 mmol), Cu(OAc)₂·H₂O (0.1 mmol), CO/O₂ = 1:7 in (1 atm), toluene (1.0 mL) and DMSO (0.1 mL) at 80 °C for 20 h. Yield is that of isolated product.



Scheme 5. Proposed mechanism.

complete the catalytic cycle.^[12b,13] H₂O is believed to be the final byproduct.

As mentioned above, the alcohol oxidation is usually a problem under oxidative conditions. As shown in Scheme 5, alcohol oxidation would normally result from the β -hydride elimination of **B**, and is usually a facile process.^[3a,12b,14] However, in this transformation, alcohol oxidation did not occur, and the product α,β -unsaturated esters were obtained in high selectivity. Thus, current reaction conditions might suppress the alcohol oxidation process. To test this hypothesis, the following experiments were carried out (Scheme 6). In the absence of CO and olefin under the standard reaction conditions, **1a** was oxidized to give a 38% yield of benzaldehyde, and the starting material was predominantly unreacted (Scheme 6). When CO or the olefin was added to the reaction system, the amount of aldehyde was reduced (Scheme 6b,c). These results indicate that alcohol oxidation is sluggish under the reaction conditions and either CO or the olefin could suppress this oxidation step. Therefore, only one equivalent of alcohol could be utilized in this transformation. It allows us to



Scheme 6. Oxidation of benzyl alcohol under different conditions. The yield was determined by HPLC and calibrated using biphenyl as the internal standard.

use a variety of functionalized primary and secondary alcohols in this oxidative carbonylative esterification.

In conclusion, we have demonstrated a palladium-catalyzed oxidative carbonylative esterification of various functionalized alcohols under base- and ligand-free conditions, wherein a CO/olefin combination was utilized as the acylating reagent with O₂ as a benign oxidant. Notably, this reaction exhibits a wide range of functional-group tolerance. Detailed mechanistic studies and the synthetic application of this methodology are currently ongoing in our laboratory.

Experimental Section

General procedure: PdCl₂ (2.7 mg, 0.015 mmol) and Cu(OAc)₂·H₂O (20 mg, 0.1 mmol) were added to a 25 mL schlenk tube equipped with a magnetic stirred bar, and a balloon filled with CO/O₂ (1:7, 1 atm) was connected to the Schlenk tube through the side arm, and purged three times. DMSO (0.1 mL), 1a (54 mg, 0.5 mmol), 2a (59 mg, 0.5 mmol), and toluene (1.0 mL) were then injected into the tube by syringe. The reaction was then heated to 80°C and stirred for 20 h. Upon completion, the reaction was quenched by ethyl acetate. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate = 50:1). The product 3aa was isolated as a white solid in 85% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.71 (d, *J* = 16.0 Hz, 1H), 7.50–7.30 (m, 7H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.25 (s, 2H), 2.37 ppm (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 167.0, 145.2, 140.8, 136.1, 131.6, 129.6, 128.6, 128.2(4), 128.1 (9), 128.1, 116.7, 66.3, 21.5 ppm.

Received: January 20, 2014

Revised: March 5, 2014

Published online: April 16, 2014

Keywords: alcohols · esterification · oxidation · palladium · synthetic methods

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