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Ligand-Controlled Palladium-Catalyzed Alkoxycarbonylation of Allenes: Regioselective Synthesis of α,β- and β,γ-Unsaturated Esters

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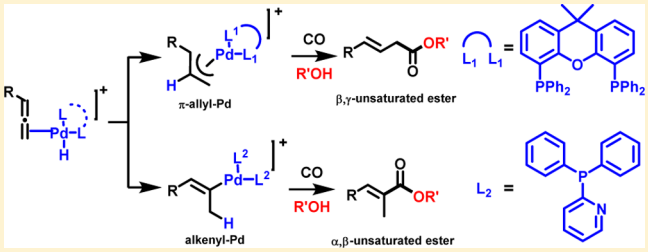
Supporting Information

ABSTRACT: The palladium-catalyzed regioselective alkoxycarbonylation of allenes with aliphatic alcohols allows to produce synthetically useful α,β- and β,γ-unsaturated esters in good yields. Efficient selectivity control is achieved in the presence of appropriate ligands. Using Xantphos as the ligand, β,γ-unsaturated esters are produced selectively in good yields. In contrast, the corresponding α,β-unsaturated esters are obtained with high regioselectivity in the presence of PPh_2Py as the ligand. Preliminary mechanistic studies revealed that these two catalytic processes proceed by different reaction pathways. In addition, this novel protocol was successfully applied to convert an industrially available bulk chemical, 1,2-butadiene, into dimethyl adipate, which is a valuable feedstock for polymer and plasticizer syntheses, with high yield and TON (turnover number).



INTRODUCTION

Carbonylation reactions are widely used in industrial production of fine and bulk chemicals as well as organic synthesis since it can efficiently introduce the synthetically versatile carbonyl group and easily expand carbon chains.[1] Within this class of reactions, transition metal catalyzed alkoxycarbonylations, also called hydroesterifications, represent a straightforward method for the conversion of widely available unsaturated compounds, CO and alcohols into the corresponding esters.[2] In this respect, catalytic alkoxycarbonylation is also of considerable interests for the synthesis of α,β- and β,γ-unsaturated carboxylic acid derivatives, which represent important intermediates, building blocks and functional molecules in organic synthesis, the chemical industry as well as biological systems.[3] Since the original work of Reppe in the past century,[2a,4] alkoxycarbonylations of π-unsaturated compounds such as alkenes,[2a,5] alkynes,[6] 1,3-dienes[5c,7] and allylic compounds[8] have been extensively studied and improved. Despite all these works, it is still highly desirable to develop catalytic systems for the straightforward, convenient, and regioselective synthesis of α,β- and β,γ-unsaturated carboxylic acid derivatives from other easily accessible start materials. Key requirements for the applicability of such methodologies are high atom-economy, broad substrate scope as well as chemo- and regioselectivity.

Compared to other available olefins, the functionalization of allenes has been only scarcely investigated over the years. Nevertheless, they have become an important class of synthon in organic synthesis, which can be applied to construct a variety of valuable molecules based on their functionalization.[9] As cumulated unsaturated species, allene is recognized that all the three carbons (C1, C2 and C3 position) on its double bonds can be the potential reaction sites.[10] This allows for various transformations at different positions on allenes. However, it also brings out a challenge to realize regioselective reactions. Although allenes functionalizations including addition reactions,[11] cyclizations,[12] oxidation[13] and reduction[14] reactions are well developed in recent years, the carbonylation of allenes is still challenging and very few examples are known.[15] This is mainly due to the above-mentioned difficult regioselectivity control of allenes, thus resulting in poor selectivity of α,β- and β,γ-unsaturated carbonylation products.[10a,15e] Taking palladium-catalyzed alkoxycarbonylations for instance, which are not known for allenes as the substrates until now,[16] there are four possible pathways for allene insertion into the Pd−H bond (Scheme 1): (1) When palladium coordinates to C1−C2 double bond, it will lead to two different insertions, from which alkenyl-Pd complex **A** and π-allyl-Pd intermediate are formed, respectively. Then, complex **A** further experiences the subsequent alkoxycarbonylation process to give the C2 carbonylation adduct **1** (α,β-unsaturated esters), while π-allyl-Pd intermediate enables an equilibration between σ-allyl-Pd species **C** and **D**, which potentially provides the C1 or C3 carbonylation adduct **2** or **3** (β,γ-unsaturated esters). (2) Alternatively, palladium coordinates to the C2−C3 double bond. Again, two different possibilities for the insertion step result, which provide alkenyl-Pd complex **B** and π-allyl-Pd

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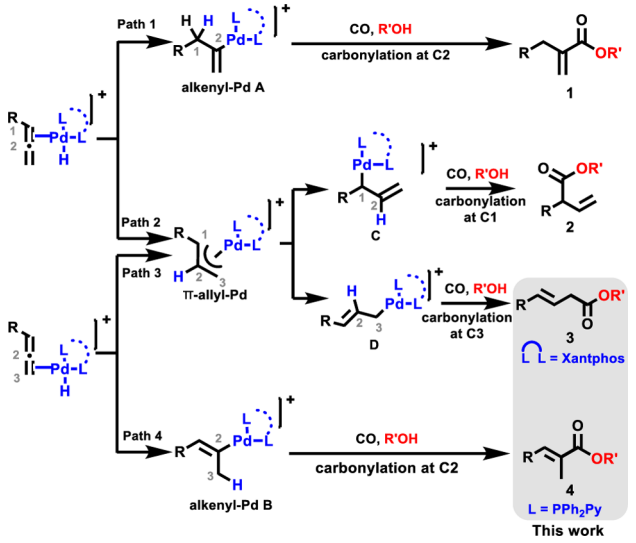
Scheme 1. Possible Pathways for Palladium-Catalyzed Allene Alkoxycarbonylation Reactions



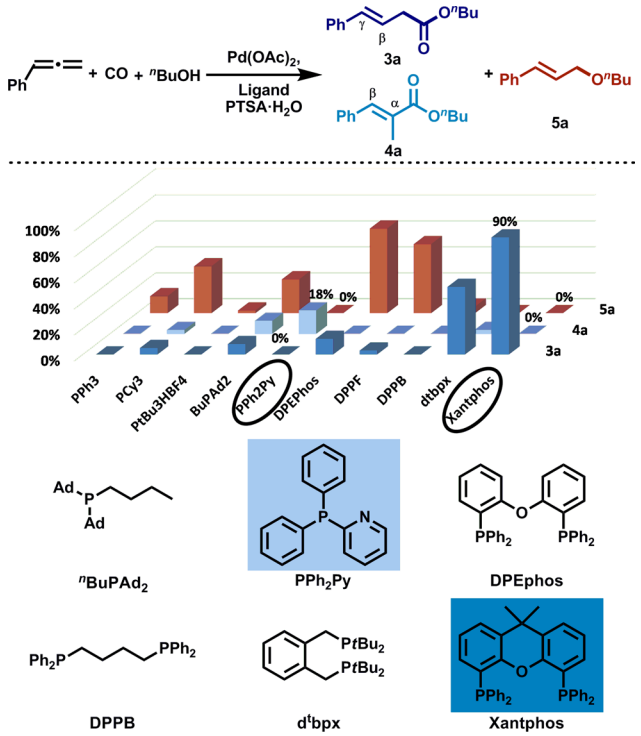
intermediate (the same species as above). The later Pd complex will form the C1 or C3 carbonylation adduct **2** or **3** (*β*,*γ*-unsaturated esters) again. Differently, C2 carbonylation adduct **4** is generated by the following alkoxycarbonylation of complex **B**.

We thought that the ligand should be able to play a key role in controlling the regioselectivity, thus leading to the generation of the *α*,*β*- or *β*,*γ*-unsaturated esters in a selective manner. On the basis of our continuing interest in the development of hydroesterification of unsaturated compounds,[7c,8e,17] we herein present the first example of palladium-catalyzed alkoxycarbonylation of allenes to synthesize *α*,*β*- and *β*,*γ*-unsaturated esters regioselectively promoted by two different ligands.

RESULTS AND DISCUSSION

Initially, we investigated the Pd-catalyzed alkoxycarbonylation of conveniently available propa-1,2-dienylbenzene **1a** and *n*-butanol **2a** as a model reaction. It is noteworthy that three products were detected in this reaction: *β*,*γ*-unsaturated esters **3a**, *α*,*β*-unsaturated esters **4a** and direct C−O coupling product **5a**. In order to improve the selectivity, we first studied the ligand effect using $Pd(OAc)_2$ as the catalyst precursor and PTSA·H_2O (*p*-toluenesulfonic acid monohydrate) as the acid cocatalyst (Scheme 2). The application of monodentate ligands, such as PPh_3, PCy_3, P^tBu_3 and $PAd_2{}^nBu$, all gave quite low catalytic activity with less than 10% yield of carbonylative products. Interestingly, when PPh_2Py was applied as the ligand, *α*,*β*-unsaturated ester **4a** was formed with high selectivity albeit only 18% yield was gained. Then, a serial of bidentate ligands were also tested. Bis[(2-diphenylphosphino)phenyl] ether (DPEphos) and 1,1,-bis(diphenylphosphino)ferrocene (DPPF) exhibited low reactivity for the carbonylation process, which mainly led to the C−O coupling product **5a**. The application of 1,4-bis(diphenylphosphino)butane (DPPB), gave worse result with less than 5% yield of the desired product. To our delight, using *α*,*α*′-bis-[di-*tert*-butylphosphino]-*o*-xylene (d^tbpx) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) as ligands, **5a** was not observed and Xantphos was identified as the most effective ligand to afford **3a** in 90% yield with excellent selectivity.

Scheme 2. Ligand Effect for the Palladium-Catalyzed Alkoxycarbonylation of Propa-1,2-Dienylbenzene 1a and *n*-Butanol 2a[a]



[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), $Pd(OAc)_2$ (1.0 mol %), monodentate ligand (4.0 mol %), bidentate ligand (2.0 mol %), PTSA·H_2O (4.0 mol %), CO (40 bar), toluene (2 mL), 110 °C, 20 h. Yields were determined by GC analysis using isooctane as the internal standard.

After optimizing the reaction conditions for the synthesis of butyl 4-phenyl-3-butenoate (see Supporting Information, Tables S1−S5), we continued to explore the scope of different allenes (Table 1). To our delight, the catalytic system can be applied in a straightforward manner to a series of aryl-substituted allenes, and good yields were obtained with substrates bearing halogen or alkyl groups at both *para* (**3b**, **3c**, **3f** and **3g**), *meta* (**3d**) and *ortho* positions (**3e**). In all these cases exclusive formation of the E-regioisomers took place. Notably, aliphatic allenes were found to be suitable substrates under similar conditions to afford the corresponding carbonylative products in moderate to good yields. As an example, cyclohexylallene participated in this carbonylation reaction with high reactivity (**3h** and **3i**). Remarkably, 1,2-butadiene, an industrial side-product from oil cracking, also reacted smoothly and gave the *β*,*γ*-unsaturated ester (**3j**) in good yield with only 0.1 mol % Pd catalyst! Moreover, electron-deficient allenes, e.g., ethyl 2,3-butadienoate, reacted smoothly and furnished a moderate yield of the desired product (**3k**). Gratifyingly, the reaction of 1,1-disubstituted allene such as 3-methyl-1,2-butadiene also furnished the desired carbonylation product in moderate yield (**3l**).

Furthermore, the reactivity of different alcohols was also investigated (Scheme 3). First, a variety of simple primary aliphatic alcohols were tested under the optimal reaction conditions. The corresponding esters were generated in good yields (**3aa** to **3af**). Moreover, secondary alcohols also underwent this transformation smoothly with excellent

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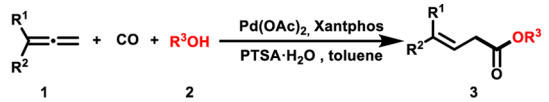
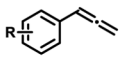
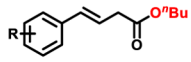
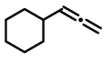
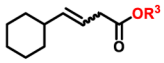
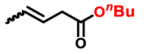
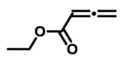
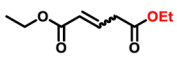
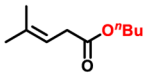
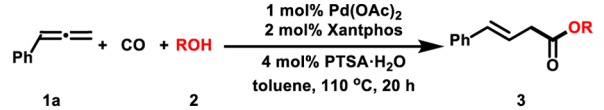
Table 1. Variation of Different Allenes for the Synthesis of β,γ-Unsaturated Esters[a]

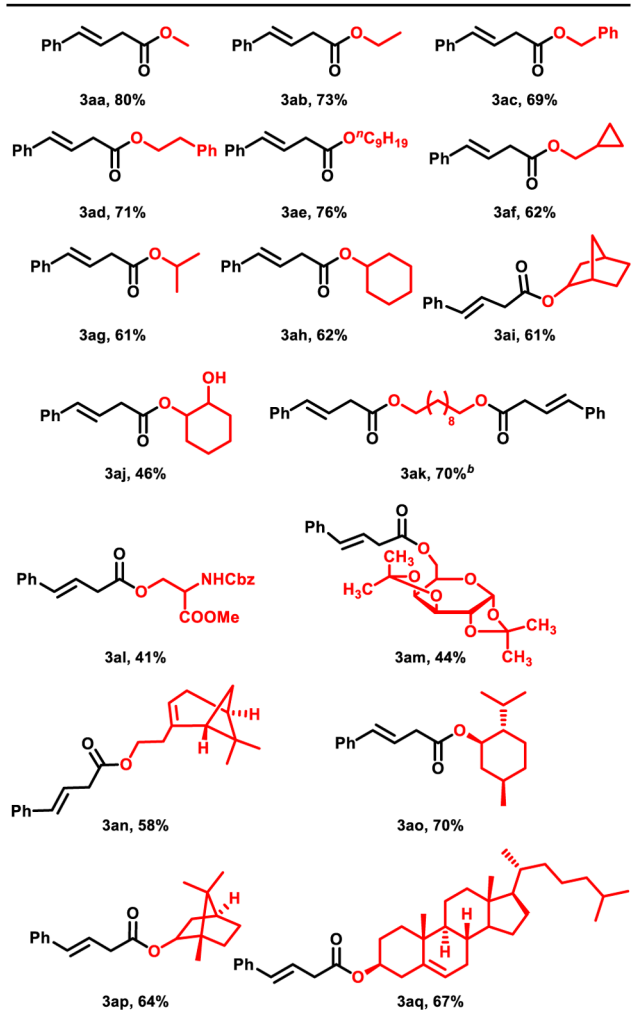


Entry	Allene	Product	Yield [%][b]
			
1	R = H	**3a**	85
2	R = 4-F	**3b**	76
3	R = 4-Cl	**3c**	79
4	R = 3-Cl	**3d**	70
5	R = 2-Cl	**3e**	76
6	R = 4-Br	**3f**	81
7	R = 4-Me	**3g**	68
			
8[c]		**3h** $R^3 = {}^n$Bu	66 (91/9)
9[c]		**3i** R^3 = Bn	63 (90/10)
			
10[d]		**3j**	76 (76/24)
			
11[c]		**3k**	65 (85/15)
			
12[e]		**3l**	57

[a]Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), $Pd(OAc)_2$ (1.0 mol %), Xantphos (2.0 mol %), PTSA·H_2O (4.0 mol %), CO (40 bar), toluene (2 mL), 110 °C, 20 h. [b]Isolated yields. *E*/*Z* ratio is shown in the parentheses and determined by GC. [c]**1** (1.0 mmol), **2** (4.0 mmol), $Pd(OAc)_2$ (1.0 mol %), Xantphos (2.0 mol %), PTSA·H_2O (4.0 mol %), CO (40 bar), toluene (2 mL), 110 °C, 20 h. [d]**1** (25 mmol), **2** (20 mmol), $Pd(cod)Cl_2$ (0.1 mol %), Xantphos (0.2 mol %), PTSA·H_2O (0.4 mol %), CO (80 bar), toluene (10 mL) in a 25 mL autoclave, 130 °C, 20 h. [e]**1** (1.0 mmol), **2** (4.0 mmol), $Pd(OAc)_2$ (1.0 mol %), Xantphos (2.0 mol %), PTSA·H_2O (4.0 mol %), CO (80 bar), toluene (2 mL), 130 °C, 20 h.

Scheme 3. Variation of Different Alcohols for the Synthesis of β,γ-Unsaturated Esters[a]





[a]Reaction conditions: **1a** (1.0 mmol), **2** (1.2 mmol), $Pd(OAc)_2$ (1.0 mol %), Xantphos (2.0 mol %), PTSA·H_2O (4.0 mol %), CO (40 bar), toluene (2 mL), 110 °C, 20 h. Isolated yield. [b]**1a** (1.5 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (1.0 mol %), Xantphos (2.0 mol %), PTSA·H_2O (4.0 mol %), CO (40 bar), toluene (2 mL), 110 °C, 20 h. Isolated yield.

regioselectivity (**3ag** to **3ai**). It is noteworthy that by tuning the amount of allenes, the mono- and dicarbonylation products of diols can be selectively formed, respectively (**3aj** and **3ak**). Interestingly, bioactive alcohols such as amino acid derivatives (**3al**) and carbohydrates (**3am**) can be used in this transformation and synthetically useful yields were obtained. Last but not the least, some natural and functionalized alcohols showed good reactivity as well. For instance, (−)-nopol (**3an**), bearing a C=C bond, proved to be suitable. Notably, secondary natural alcohols, such as menthol (**3ao**), (−)-borneol (**3ap**), and cholesterol (**3aq**) participated in this transformation efficiently highlighting the broad substrate scope of this protocol and its potential utility in organic synthesis.

In order to gain some mechanistic insights into this reaction, a deuterium labeling experiment was carried out. When methanol-d_4 was applied in this transformation, 68% of the ester product was D-labeled only at the β-position along with 32% nonlabeled product (eq 1). The proton at the β-position in nonlabeled product might be introduced from acid cocatalyst and trace amount of water in the solvent. Therefore, deuterated acid TsOD·D_2O was employed as well, and 8% of deuterated ester product at C2 position was obtained (eq 2) which indicates a partial scrambling process. Nevertheless, these

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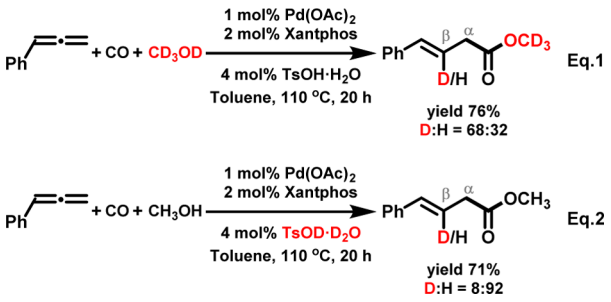


results demonstrate a selective insertion of the double bond between C2 and C3 positions of allene into the Pd−D or Pd−H bond and the β,γ-unsaturated ester products were not generated via isomerization of preformed α,β-unsaturated isomers as mentioned in Scheme 1.

Next, the kinetic progress of the reaction between propa-1,2-dienylbenzene **1a** and *n*-butanol **2a** was examined under the optimal conditions (Figure 1). It is shown that **1a** is initially

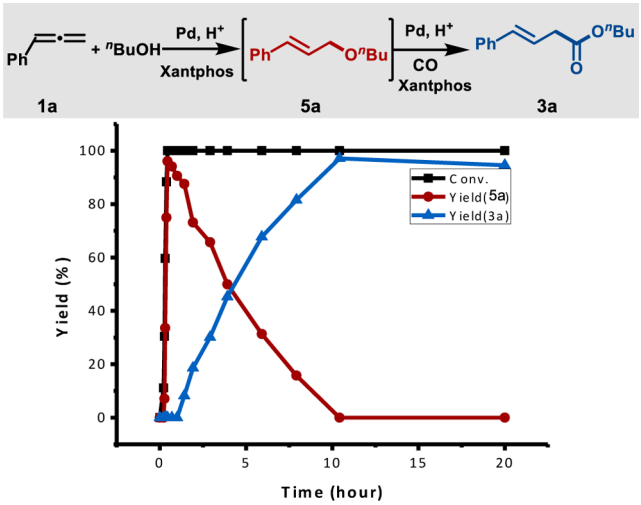
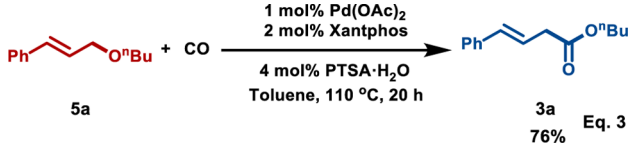


Figure 1. Kinetic profile for the carbonylation reaction of **1a** and **2a** for the synthesis of β,γ-unsaturated esters.

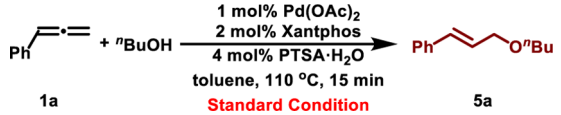
converted into the C−O coupling product **5a**. Then, the β,γ-unsaturated ester **3a** is generated at a lower reaction rate along with the consumption of the reaction intermediate **5a**. This observation is well in accordance with our previous study for the alkoxycarbonylation of allylic alcohols.[8e] It illustrates that a common reaction intermediate, π-allyl-Pd species, is involved in these two reactions, which is more prone to undergo nucleophilic addition with aliphatic alcohols compared to the slow CO insertion step.

In order to confirm whether **5a** is an intermediate in this carbonylation reaction, it was applied to the standard conditions and the corresponding β,γ-unsaturated ester **3a** was obtained with 76% yield (eq 3). This result revealed that **5a** should be a reaction intermediate in this carbonylation process.



To further verify that the direct C−O coupling process is catalyzed by palladium and acid cocatalyst, three control experiments were carried out. As shown in Table 2, under the

Table 2. Control Experiments for the Formation of the Allylic Ether 5a

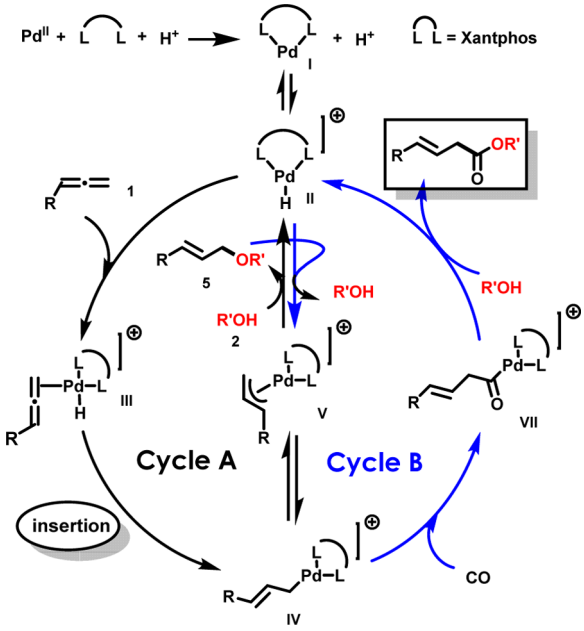


entry	variation from "standard condition"	conv. [%]	yield [%]
1	none	79	77
2	without [Pd] and Xantphos	0	–
3	without PTSA·H_2O	0	–

standard conditions, the direct C−O coupling product **5a** is obtained in 77% yield after 15 min. However, in the absence of either Pd catalyst or PTSA·H_2O, there was no conversion of starting material **1a** at all.

On the basis of all these experimental findings, the following mechanism is proposed for the synthesis of β,γ-unsaturated esters (Scheme 4). Initially, Pd(II) catalyst precursor is in situ

Scheme 4. Proposed Mechanism for the Synthesis of β,γ-Unsaturated Esters (L,L = Xantphos)



reduced to Pd(0) species **I** in the presence of excess amount of phosphine ligands.[18] In the presence of acid, this complex is in an equilibrium with the corresponding Pd(II) hydride complex **II**, which are both key catalytically active species to initiate the following domino catalytic cycles.[8e,17d] The allene substrate **1** coordinates to Pd−H species to form the Pd complex **III**, and consequent insertion of C2−C3 double bond will give σ- and π-allyl-Pd intermediates **IV** and **V**. These intermediates undergo a fast nucleophilic substitution by the aliphatic alcohol **2** at the less sterically hindered terminal position to afford the C−O coupling product **5** and regenerate Pd hydride species **II** to finish cycle A. Subsequently, in the presence of acid, **5** is activated and reacts with Pd(0) species **I** via oxidative addition to form reaction intermediates **V** and **IV** again. Then, complex

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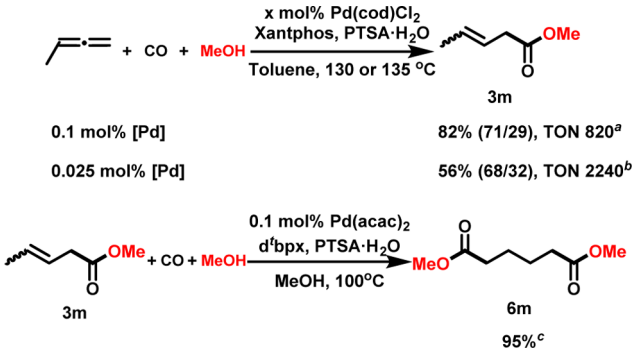
IV experiences a CO insertion process to afford acyl Pd species **VII**. Finally, the alcoholysis of intermediate **VII** provides the desired carbonylation product β,γ-unsaturated esters **3** and regenerates Pd hydride species **II**. Although we could not exclude the reaction path 2 (Scheme 1), which can also lead to the same product in this reaction, we prefer the shown mechanistic proposal. Considering the steric effect at C1 position of the different allenes, it is more likely that the less steric hindered double bond coordinates to the Pd center bearing the bulky ligand Xantphos and delivers the thermodynamically more stable reaction intermediate **III**.

Furthermore, we were interested in demonstrating the utility of this method for the synthesis of an industrially important building block. 1,2-Butadiene is a minor product from oil cracking which is available from industry on multitons-scale. To the best of our knowledge no catalytic applications have been described of this feedstock in the open literature. Indeed, we succeeded to convert 1,2-butadiene into dimethyl adipate **6m**, which is a valuable start material for polymer and plasticizer synthesis, in two steps (Scheme 5). The first alkoxycarbonylation reaction takes place with only 0.1 mol % Pd catalyst loading to give the β,γ-unsaturated esters **3m** with a turnover number (TON) of 820. Further decrease of the Pd catalyst loading led to a TON of even 2240. Subsequent transformation of **3m** gave selectively dimethyl adipate **6m** in high yield via the second alkoxycarbonylation step based on a known isomerization carbonylation catalyst system.[7c]

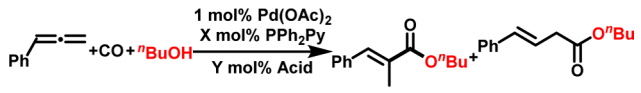
Scheme 5. Synthetic Application by Using 1,2-Butadiene as the Substrate



[a]Reaction conditions: 1,2-butadiene (20−25 mmol), methanol (20 mmol), $Pd(cod)Cl_2$ (0.1 mol %), Xantphos (0.2 mol %), PTSA·H_2O (0.4 mol %), CO (80 bar), toluene (10 mL), 130 °C, 20 h. GC yield. *E*/*Z* ratio is shown in the parentheses and determined by GC. [b]Reaction conditions: 1,2-butadiene (20−25 mmol), methanol (20 mmol), $Pd(cod)Cl_2$ (0.025 mol %), Xantphos (0.05 mol %), PTSA·H_2O (0.1 mol %), CO (80 bar), toluene (10 mL), 135 °C, 72 h. GC yield. *E*/*Z* ratio is shown in the parentheses and determined by GC. [c]Reaction conditions: **3m** (10 mmol), methanol (10 mL), $Pd(acac)_2$ (0.1 mol %), dtbpx (0.4 mol %), PTSA·H_2O (0.8 mol %), CO (40 bar), 100 °C, 20 h. GC yield.

As we discussed above (Scheme 2), it is interesting to note that in the presence of PPh_2Py as ligand a good selectivity for the synthesis of the other regioisomer **4a** is observed, albeit in a low yield. This result intrigued us to vary the reaction conditions to improve the yield of this transformation. As shown in Table 3 the performance of the catalyst is influenced by the different acid cocatalysts. TFA (trifluoroacetic acid) showed superior reaction activity compared to other tested acid cocatalysts including PTSA·H_2O, CH_3SO_3H and CF_3SO_3H (Table 3, entries 1−4). Then, the effects of ligand and cocatalyst concentrations were investigated as well. Actually, both the concentrations of the acid cocatalyst TFA and the ligand have a profound influence on the yield of **4a** (Table 3, entries 5−9). To our delight, under optimized conditions the desired product **4a** is obtained in 75% yield (entry 8) along with 7% of **3a** as byproduct. However, a higher loading of the acid cocatalyst compressed the reaction efficiency (entry 9).

Table 3. Effect of Acid Cocatalyst and Ligand for the Synthesis of 4a[a]



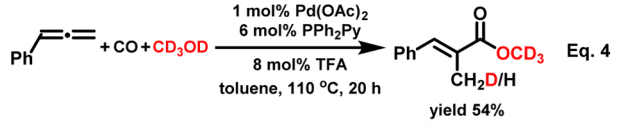
1a 2a 4a 3a

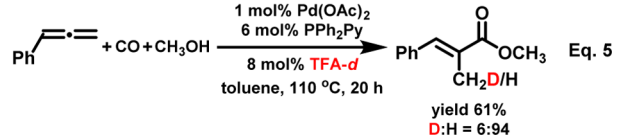
entry	acid	X:Y	yield **4a** [%]	yield **3a** [%]
1	PTSA·H_2O	4:4	18	trace
2	CH_3SO_3H	4:4	20	trace
3	CF_3SO_3H	4:4	4	trace
4	TFA	4:4	44	4
5	TFA	4:5	43	5
6	TFA	4:6	49	5
7	TFA	6:6	56	7
8	**TFA**	**6:8**	**75**	**7**
9	TFA	6:10	66	11

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), $Pd(OAc)_2$ (1.0 mol %), PPh_2Py (X mol %), Acid (Y mol %), CO (40 bar), toluene (2.0 mL), 110 °C, 20 h. GC yield.

With the optimal conditions established, various alcohols **2** were employed to react with allenes **1** to produce the corresponding α,β-unsaturated esters **4** (Scheme 6). All tested primary aliphatic alcohols gave the desired carbonylation product in good yields (**4a** to **4e**). Interestingly, some bioactive secondary alcohols were also compatible in this transformation and moderate yields were obtained (**4f** and **4g**). Then, different allenes were investigated in this transformation as well: 4-methyl phenyl substituted allene worked well under the standard conditions (**4h**); remarkably, aliphatic allenes including cyclohexylallene (**4i**), and 1,2-butadiene (**4k**) gave the corresponding ester product in moderate to good yields. Finally, it is worth noting that a functionalized substrate, ethyl 2,3-butadienoate (**4j**), underwent this transformation smoothly as well.

Regarding the mechanism a similar deuterium labeling experiment was carried out. When methanol-d_4 was applied to this reaction, 76% of the ester product was deuterated only at C3 position along with 24% nonlabeled product (eq 4).





Additionally, using TFA-*d* instead of TFA gave 6% of deuterated ester product at C3 position (eq 5). These results indicate that the double bond between C2 and C3 positions

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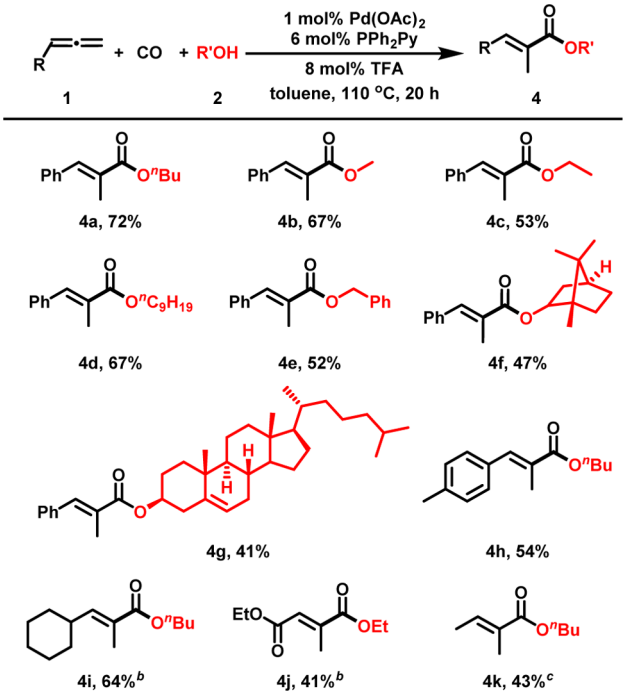
Scheme 6. Scope of Different Allenes 1 and Alcohols 2 for the Synthesis of α,β-Unsaturated Esters 4[a]



[a]Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), $Pd(OAc)_2$ (1.0 mol %), PPh_2Py (6.0 mol %), TFA (8.0 mol %), CO (40 bar), toluene (2 mL), 110 °C, 20 h. Isolated yields. [b]**1** (1.0 mmol), **2** (4.0 mmol), $Pd(OAc)_2$ (1.0 mol %), PPh_2Py (6.0 mol %), TFA (8.0 mol %), CO (40 bar), toluene (2 mL), 110 °C, 20 h. Isolated yields. [c]**1** (18 mmol), **2** (20 mmol), $Pd(cod)Cl_2$ (0.2 mol %), PPh_2Py (1.2 mol %), TFA (1.6 mol %), CO (80 bar), toluene (10 mL) in a 25 mL autoclave, 130 °C, 20 h. Isolated yields.

inserts into the Pd−D or Pd−H bond in a reverse manner compared to the synthesis of β,γ-unsaturated esters, and the carbonylation products are not generated via the isomerization of other isomers as well.

In order to confirm whether the C−O coupling reaction intermediate is involved in this transformation, the kinetic progress was also examined under the optimal conditions. As is shown in Figure 2, the corresponding C−O coupling product was not observed during the whole reaction process. The carbonylation product **4a** was accumulated from the very beginning along with the gradual consumption of the allene substrate **1a**.[19] This result proves that this reaction undergoes a mechanistically different reaction pathway compared to the synthesis of the β,γ-unsaturated esters.

On the basis of this experimental observation, a possible reaction pathway is proposed for the synthesis of α,β-unsaturated esters. As shown in Scheme 7, the catalyst precursor leads to an equilibrium of the active Pd(0) species **I** with the Pd(II) hydride complex **II**.[18] Then, allene **1** coordinates to Pd to form the complex **III**, and subsequent double bond insertion in a reverse manner affords the alkenyl-Pd intermediate **VIII** instead of π-allyl-Pd intermediate formed in the previous example.[20] Therefore, in contrast to the reaction pathway for the formation of β,γ-unsaturated esters, the direct C−O coupling product was not observed in this case as the reaction intermediate (the reaction process shown in gray color in Scheme 7). It is due to the difficult C−O bond reductive elimination between alkenyl and alkoxyl groups.[21] Then, Pd

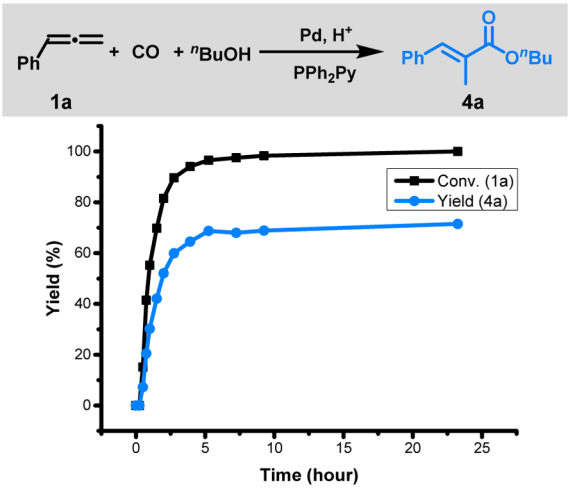
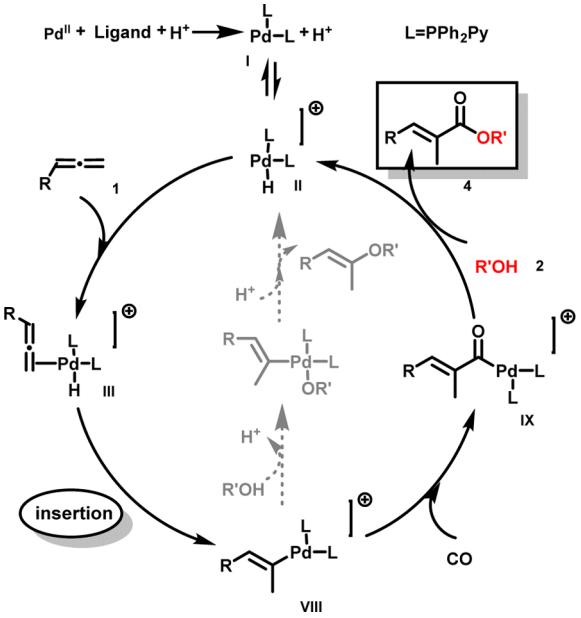


Figure 2. Kinetic profile for the carbonylation reaction of **1a** and **2a** for the synthesis of α,β-unsaturated esters.

Scheme 7. Proposed Mechanism for the Synthesis of α,β-Unsaturated Esters



complex **VIII** directly undergoes a facile CO insertion process to give the corresponding acyl Pd species **IX**. Finally, alcoholysis of intermediate **IX** generates the desired product α,β-unsaturated esters **4** and closes the catalytic cycle.

CONCLUSIONS

In summary, we have developed the first general carbonylation reaction of allenes with aliphatic alcohols to produce a variety of synthetically useful unsaturated esters. Depending on the ligand present, α,β- and β,γ-unsaturated esters are selectively formed. Interestingly, these two catalytic reactions proceeded via different reaction pathways supported by mechanistic studies. Moreover, the first catalytic reactions of the industrially available 1,2-butadiene are described. The valuable building block dimethyl adipate was obtained in high yield at low catalyst loadings. These procedures are expected to complement the current methods for carbonylation reactions in organic synthesis.

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■ ASSOCIATED CONTENT

Supporting Information

Additional experimental results and procedures and characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04052.

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Notes

The authors declare no competing financial interest.

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(19) Although the conversion of **1a** is nearly 100%, the yield of product was only 70%. Apart from the corresponding isomer **3a** (7% yield, detected by GC), the other by-product was not observed from GC. We think allene is polymerized or decomposed under the reaction conditions. For the related polymerization of allenes, see: Osakada, K.; Takeuchi, D. Coordination Polymerization of Dienes, Allenes, and Methylenecycloalkanes. In *Polymer Synthesis*; Springer: Berlin, 2004; Vol. *171*, pp 137−194.
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■ NOTE ADDED AFTER ASAP PUBLICATION

Scheme 2 was corrected on July 8, 2015.

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