

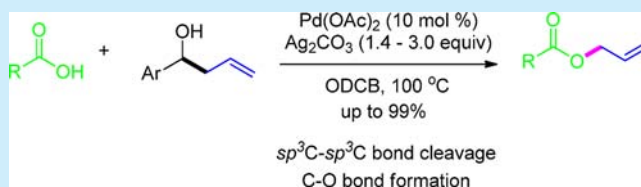
Palladium-Catalyzed Allylic Esterification via C–C Bond Cleavage of a Secondary Homoallyl Alcohol

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Supporting Information

ABSTRACT: Palladium-catalyzed allylic esterifications of secondary homoallyl alcohols with acids via sequential retro-allylation and esterification are demonstrated, affording the corresponding allyl ester in up to 99% yield. The electron effect of the substituent of the secondary alcohol was found to be crucial to the selective C–C bond cleavage.



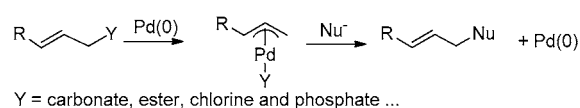
Transition-metal-catalyzed C–C bond activation has been an emerging area which provides new modes of chemical reactivity to synthetic organic chemistry. The strategies mainly involving three- or four-membered ring strain release,¹ aromatization,² and chelation assistance³ have been reported to activate inert C–C bonds.⁴ However, activation of $sp^3\text{C}-sp^3\text{C}$ in unstrained molecules is less reported.⁵ Tertiary homoallyl alcohols were successfully applied as substrates for selective unstrained $sp^3\text{C}-sp^3\text{C}$ bond cleavage via retro-allylation,^{6,7} forming a stable π -allyl metal intermediate which is suitable for subsequent transformation with aryl halides,⁸ aldehydes,⁹ cinnamyl acetate,¹⁰ and acrylate ester.¹¹ In comparison, secondary homoallyl alcohols have rarely been employed in such transformations.⁹ There have been a few reports with respect to C–C cleavage of secondary alcohols.¹² For instance, Chiba's group reported azide assisting the C–C bond cleavage of cyclic secondary 2-azidoalcohols.^{5b} Shi and co-workers demonstrated some examples of C–C bond cleavage of secondary alcohols through Rh(III)-catalyzed β -carbon elimination with the pyridinyl group as a directing group.¹³

On the other hand, Pd-catalyzed allylic esterification has always been a challenging research area due to the high reactivity problem of the resulting allylic esters toward the metal catalysts.¹⁴ Installation of a prefunctionalized group at the allylic position for the generation of a key π -allyl Pd intermediate is a prerequisite in traditional allylic esterification (Tsuji–Trost reaction).¹⁵ The functionalized groups include carbonate,^{14a,16} ester,^{14b,17} chlorine,^{14d,18} and phosphate¹⁹ (Scheme 1a). Oxidative allylic C–H bond esterification has also been realized in recent years (Scheme 1b).²⁰ However, to the best of our knowledge, transition-metal-catalyzed allylic esterification via selective C–C bond cleavage has not been documented.

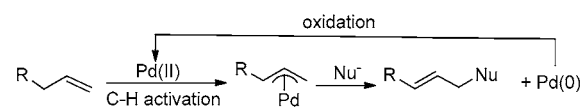
Herein we report an unprecedented Pd(II)-catalyzed sequential selective C–C bond cleavage of a secondary homoallyl alcohol and esterification with acids as nucleophiles (Scheme 1c). The major challenge in cleaving the C–C bond adjacent to a secondary alcohol is to suppress β -H elimination

Scheme 1. π -Allyl Pd Formation and Esterification

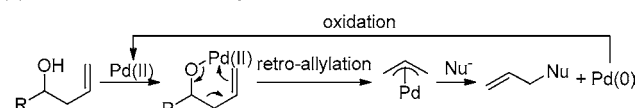
(a) Traditional Allylic Esterification



(b) Oxidative Allylic C–H Bond Esterification



(c) This work: Oxidative Allylic C–C Bond Esterification

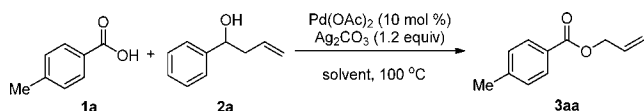


which is the typical transformation of secondary alcohols in transition metal catalytic systems.²¹ This strategy would provide a new model for allylic substitution reaction.

We initiated our studies by examining the reactivity of β -phenylbut-3-en-1-ol (**2a**) with 4-methylbenzoic acid (**1a**) in the presence of 10 mol % of Pd(OAc)₂ and 1.2 equiv of Ag₂CO₃ in toluene. To our delight, the reaction went smoothly at 100 °C for 24 h to afford the desired allyl 4-methylbenzoate (**3aa**) in 44% GC yield (Table 1, entry 1). Other oxidants such as AgF, AgOAc, Ag₂O, and Cu(OAc)₂ were found to be less efficient for the reaction, and lower yields of **3aa** were obtained (Table 1, entries 2–5, and Supporting Information Table S1). Then we investigated various solvents including DMSO, DMF, ODCB (1,2-dichlorobenzene), and PhCF₃ (Table 1, entries 6–9). While all the tested solvents could be tolerated, the reaction in ODCB gave the superior yield (57%) (Table 1,

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Table 1. Optimization of Reaction Conditions^a


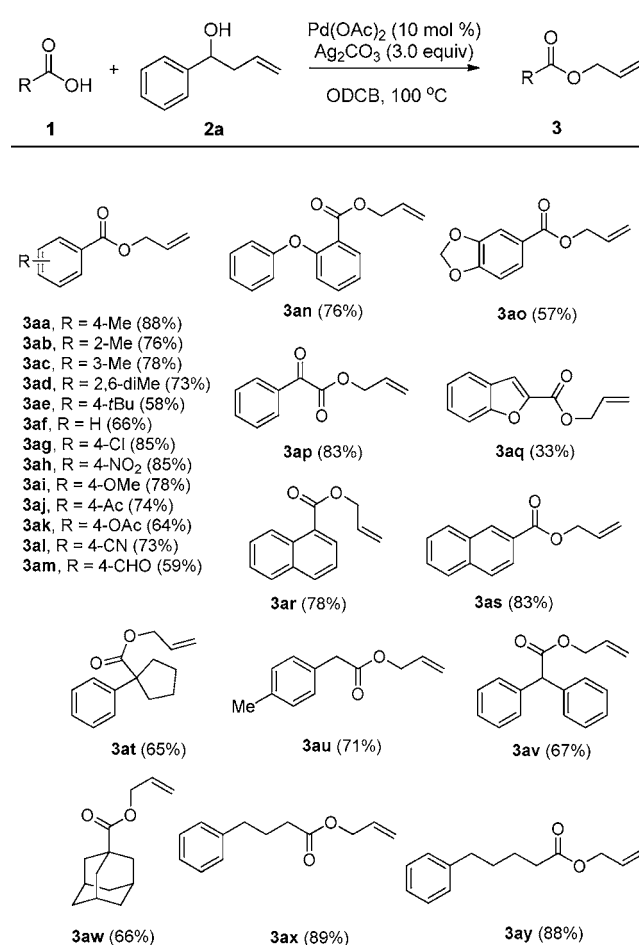
entry	oxidant	solvent	time (h)	yield (%) ^b
1	Ag ₂ CO ₃	toluene	24	44
2	AgF	toluene	24	12
3	AgOAc	toluene	24	15
4	Ag ₂ O	toluene	28	20
5	Cu(OAc) ₂	toluene	29	9
6	Ag ₂ CO ₃	DMSO	33	32
7	Ag ₂ CO ₃	DMF	33	19
8	Ag ₂ CO ₃	ODCB ^f	50	57
9	Ag ₂ CO ₃	PhCF ₃	50	56
10 ^c	Ag ₂ CO ₃	ODCB	50	80(77) ^e
11 ^d	Ag ₂ CO ₃	ODCB	24	91(88) ^e

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), Pd(OAc)₂ (10 mol %), oxidant (0.36 mmol), solvent (2 mL). ^bGC yield using dodecane as internal standard. ^cOxidant (0.9 mmol). ^d**2a** (0.9 mmol), oxidant (0.9 mmol). ^eIsolated yield in parentheses. ^fODCB = 1,2-dichlorobenzene.

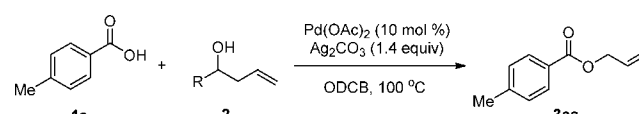
entry 8). Further investigation revealed that increasing the amount of Ag₂CO₃ (3 equiv) and **2a** (3 equiv) could deliver the best yield of **3aa** (88% isolated yield) (Table 1, entry 11).

Under the optimal reaction conditions (10 mol % of Pd(OAc)₂, 3 equiv of Ag₂CO₃, 3 equiv of **2a**, ODCB (0.15 M), 100 °C) (Table 1, entry 11), a variety of acids **1** were examined to evaluate the generality of the reaction. The results were summarized in Scheme 2. First, different substituted benzoic acids were tested. In general, benzoic acids bearing an alkyl group on different positions of the phenyl ring could be tolerated in reaction conditions (58%–88%, **3aa**–**3ae**). For the substrates with an electron-withdrawing (**3ag**, **3ah**) and electron-donating group (**3ai**, **3an** and **3ao**) on the phenyl ring, the reaction went smoothly to afford the desired products in good yields. It is worth noting that various functionalities including acetyl (**3aj**), acetoxyl (**3ak**), nitrile (**3al**), and formyl (**3am**) groups were tolerated in optimal reaction conditions. Moreover, benzoylformic acid worked well, affording allyl benzoylformate **3ap** in 83% yield. This procedure also proceeded smoothly with naphthoic acid **3ar** and **3as** as substrates. We further examined aliphatic acid as substrates and found all of them deliver corresponding products in good yields (**3at**–**3ay**). Heterocyclic carboxylic acid gave product **3aq** in a lower yield (33%) due to part of the substrate decomposing under the reaction conditions.

The reactivities of a variety of homoallyl alcohols were further surveyed (Table 2). Our studies indicated an electron-rich aromatic substituent improved the reactivity of the C–C bond cleavage.²² Under the optimal reaction conditions, by employing 2,4-dimethoxy substituted **2b** as a substrate, **3aa** was obtained in 99% GC yield. In light of this observation, we attempted to reduce the consumption of **2** and Ag₂CO₃. The reaction of **1a** with 1.2 equiv of **2b** afforded the corresponding product **3aa** in 99% yield (Ag₂CO₃, 2.0 equiv) and 93% yield (Ag₂CO₃, 1.4 equiv), respectively (Table 2, entry 1). These findings revealed that β-H elimination was well suppressed when the substrate with an electron-rich aromatic ring adjacent to the hydroxyl group was employed. Further substrate investigation was conducted under these reaction conditions:

Scheme 2. Palladium(II)-Catalyzed Retro-Allylation and Esterification of **2a** with Acids^{a,b}

^aReaction conditions: **1** (0.3 mmol), **2a** (0.9 mmol), Pd(OAc)₂ (10 mol %), Ag₂CO₃ (0.9 mmol), ODCB (2 mL), 24 h. ^bIsolated yield.

Table 2. Palladium(II)-Catalyzed Retro-Allylation and Esterification of **2** with Acid **1a**^a


entry	2/R	yield (%) ^b
1	2b /2,4-(OMe) ₂ -C ₆ H ₃	99 (93) ^c
2	2c /4-OMe-C ₆ H ₄	71
3	2d /2,3,4-(OMe) ₃ -C ₆ H ₂	72
4	2e /3,4,5-(OMe) ₃ -C ₆ H ₂	59
5	2f /2,4,6-(OMe) ₃ -C ₆ H ₂	9
6	2g /4-NO ₂ -C ₆ H ₄	8

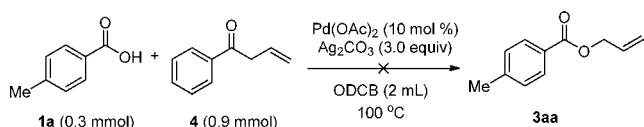
^aReaction conditions: **1a** (0.3 mmol), **2** (0.36 mmol), Pd(OAc)₂ (10 mol %), Ag₂CO₃ (0.42 mmol), ODCB (2 mL), 24 h. ^bGC yield using dodecane as internal standard. ^cAg₂CO₃ (0.6 mmol).

10 mol % of Pd(OAc)₂, 1.4 equiv of Ag₂CO₃, 1.2 equiv of **2**, ODCB (0.15 M), 100 °C. When the phenyl ring was *p*-methoxy substituted (**2c**), 2,3,4-trimethoxy substituted (**2d**), and 3,4,5-trimethoxy substituted (**2e**), slightly decreased yields were afforded (Table 2, entries 2–4). The substrate **2f** with a 2,4,6-trimethoxy substituent on the phenyl ring only gave a 9% GC yield mainly due to the steric hindrance effect (Table 2,

entry 5). Substrate **2g** with a nitro group barely provided product in 8% yield (Table 2, entry 6).

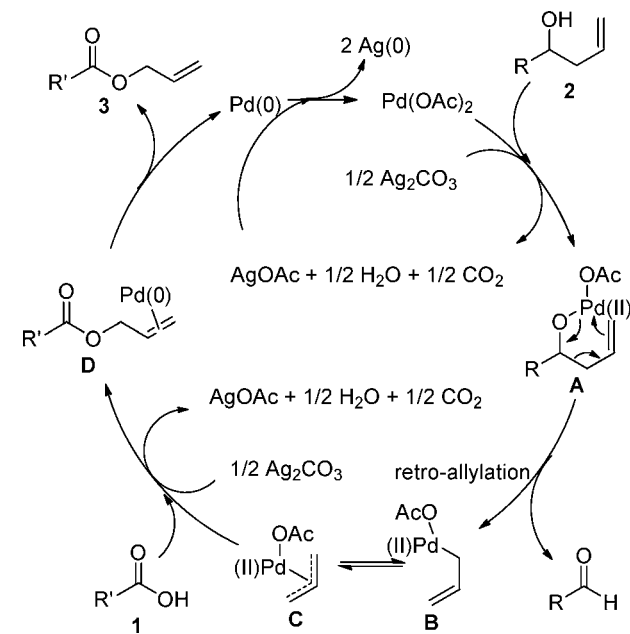
A controlled experiment was conducted with allyl ketone **4** instead of allyl alcohol **2a** to investigate whether the oxidation product **4** via β -H elimination from a secondary homoallyl alcohol could be transferred to desired product **3aa**. The result showed no desired product was obtained under such reaction conditions, which ruled out the possibility of generating desired product **3aa** from the byproduct **4** (Scheme 3).

Scheme 3. Reaction between 1a and 4 under the Optimal Reaction Conditions



Based on the above studies, a plausible mechanism has been proposed for this Pd(II)-catalyzed sequential C–C bond cleavage of a secondary homoallyl alcohol and esterification reaction (Scheme 4). Before the Pd(II) catalyst coordinates

Scheme 4. Plausible Mechanism



with secondary homoallyl alcohol **2** to form the intermediate **A**, Ag_2CO_3 might act as a base to facilitate the deprotonation of **2**.^{8a} π -allyl Pd intermediate **B** or **C** was generated from **A** via retro-allylation. Subsequently, the intermediate **B** underwent esterification with acid **1** to form the desired product **3**. Pd(0) was formed via reductive elimination from intermediate **D**. The Pd(II) species, oxidized by Ag_2CO_3 , was regenerated for the next catalytic cycle.

In conclusion, we have demonstrated the $\text{Pd}(\text{OAc})_2$ catalyzed allylic esterification of secondary homoallyl alcohols with acids via sequential retro-allylation and esterification, affording a corresponding allyl ester in good yields. In this transformation, a C–C bond was selectively cleaved preferentially from electron-rich aromatic substituted homoallyl alcohols. A plausible Pd(II)/Pd(0) mechanism was proposed. This strategy provides a new concept to generate a π -allyl Pd

intermediate via C–C bond cleavage for the allylic substitution reaction. Further studies on other transformations based on this concept are ongoing in our laboratory, and the results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Procedures and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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