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Palladium-Catalyzed Oxidative Rearrangement of Tertiary Allylic Alcohols to Enones with Oxygen in Aqueous Solvent

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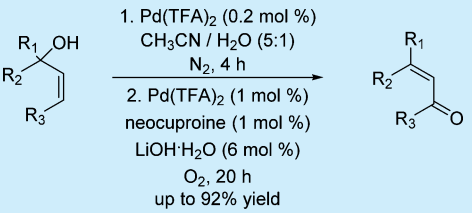
Supporting Information

ABSTRACT: A one-pot procedure for $Pd(TFA)_2$-catalyzed 1,3-isomerization of tertiary allylic alcohols to secondary allylic alcohols followed by a $Pd(TFA)_2$/neocuproine-catalyzed oxidative reaction to β-disubstituted-α,β-unsaturated kenones was developed.



The broad utility of β-disubstituted α,β-unsaturated ketones **D** (Figure 1) in organic synthesis[1] has continued to attract considerable synthetic efforts to develop more efficient methods for these ketones' syntheses.[2] The alkylative carbonyl transposition of β-disubstituted α,β-unsaturated carbonyl compounds (Figure 1), which entails a 1,2-addition of **A** by organometallic reagents to form **B**, followed by isomerization of tertiary allylic alcohol **B** to **C**, and oxidation of **C** to the corresponding β-disubstituted α,β-unsaturated ketones **D**, represents a practical strategy that extends the synthetic latitude of this transformation.

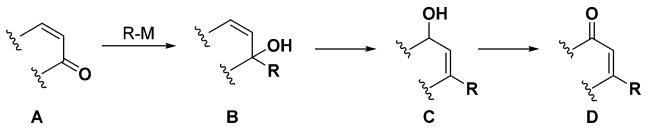


Figure 1. Alkylative carbonyl transposition of β-disubstituted α,β-unsaturated ketones.

The oxidative rearrangement of tertiary allylic alcohols to β-disubstituted α,β-unsaturated carbonyl compounds has been explored intensively, and some representative examples include (1) oxochromium(VI)-based reagents (Collins reagent, PCC or PDC);[3] (2) 2-iodoxybenzoic acid (IBX)-based oxidative rearrangement of tertiary allylic alcohols;[4] (3) TEMPO-derived oxoammonium salts as oxidative reagents;[5] (4) 2-iodoxybenzenesulfonic acid (IBS)-catalyzed oxidative rearrangement of tertiary allylic alcohols to enones with oxone;[6] and (5) copper-catalyzed aerobic oxidative rearrangement of tertiary allylic alcohols.[7] Recently, Pt-black has also been reported to be an effective agent to catalyze the oxidative rearrangement of tertiary allylic alcohols to afford enones using aqueous hydrogen peroxide as an oxidant.[8]

Pd-catalyzed allylation with allylic alcohols as substrates has been widely utilized for the construction of C−C and C−N bonds in organic synthesis,[9] and the catalytic conversion of allylic alcohols has been examined in most cases through in situ activation of a hydroxy group with the aid of Lewis acids (e.g., $Ti(OPr^i)_4$, BEt_3, BPh_3, and $SnCl_2$)[10] or by conversion into the esters of inorganic acids (e.g., As_2O_3, B_2O_3, and CO_2).[11] It is noteworthy that these reactions are usually carried out in organic solvents. A challenging question, from both an economical and an environmental point of view, is if such a sequential transformation could be achieved based on allylic alcohol in aqueous solution under aerobic conditions. We hypothesized that Pd-catalyzed 1,3-isomerization of allylic alcohols[12−17] in the absence of Lewis acid or activating agents in aqueous solution followed by Pd-catalyzed aerobic oxidation of the resultant allylic alcohols would allow us to achieve a direct Pd-catalyzed oxidative rearrangement of allylic alcohols[18] to their corresponding β-disubstituted α,β-unsaturated ketones in a one-pot reaction fashion[19] (Figure 1, **B** to **D**). Herein, we report our discovery of a Pd-catalyzed oxidative rearrangement of tertiary allylic alcohols under aerobic conditions, yielding the corresponding enals or enones in good to excellent yields.

Our initial effort toward the proposed chemistry was to search for optimized reaction conditions to achieve 1,3-isomerization of allylic alcohols. We tested several Pd catalysts in different solvents (Table 1). Among the catalysts we screened, $Pd(TFA)_2$ (1 mol %) was proved to be the best catalyst when the reaction was carried in a mixed solvent of

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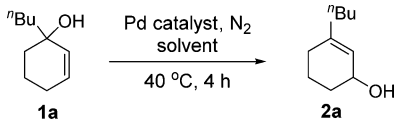
Table 1. Evaluation of Catalytic Conditions[a]



1a 2a

entry	catalyst	loading (mol %)	solvent	yield[b]/conv (%)
1	$Pd(MeCN)_4(BF_4)_2$	1	toluene	<5
2	$Pd(MeCN)_4(BF_4)_2$	1	CH_2Cl_2	<5
3	$Pd(MeCN)_4(BF_4)_2$	1	CH_3CN	<5
4	$Pd(MeCN)_4(BF_4)_2$	1	CH_3CN/H_2O (5:1)	46 (94)
5	$Pd(OAc)_2$	1	CH_3CN/H_2O (5:1)	no reaction
6	$Pd_2(dba)_3$	1	CH_3CN/H_2O (5:1)	no reaction
7	$PdCl_2$	1	CH_3CN/H_2O (5:1)	<5
8	$Pd(TFA)_2$	1	CH_3CN/H_2O (5:1)	85 (92)
9	$Pd(TFA)_2$	0.2	CH_3CN/H_2O (5:1)	82 (88)

[a]Reactions were conducted with **1a** (0.5 mmol) in solvent (2.5 mL). [b]Isolated yields.

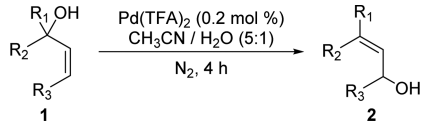
CH_3CN/H_2O (entry 8). When the catalyst loading was reduced to 0.2 mol %, no significant decrease of the reaction yield was observed (entry 9). Interestingly, when $Pd(MeCN)_4(BF_4)_2$ was used as in organic solvents including toluene, dichloromethane, or acetonitrile, only a trace amount of isomerized product **2a** was observed (entries 1−3). However, when the reaction was carried out in a mixed solvent of CH_3CN and water, 46% yield was obtained (entry 4).

The scope and limitation of this catalytic system are demonstrated in Table 2. Five-, six-, and seven-membered-ring based cyclic substrates readily responded to give the expected β-disubstituted α,β-unsaturated ketones in good to excellent yields (Table 2, entries 1−15). In particualr, five-membered substrates were relatively reactive and could carry out the rearrangement reaction at 0 °C. It is also worthwhile to mention that when the substrate had a substituent at the 3-position, the product yield decreased presumably because of the substrate's steric effect (entry 11). Several acyclic tertiary allylic alcohols (entries 16−18) were also examined. Although the expected rearrangement could proceed, both temperature and catalyst loading are necessary to increase to achieve relative good yields. The reaction of furan-substituted substrate **1t** occurred in excellent yield (entry 19). However, the nitrogen-containing heterocycle substrate **1u** gave no desired product, probably due to the deactivation of palladium catalyst caused by the strongly coordinating effect of nitrogen atom (entry 20).

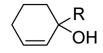
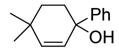
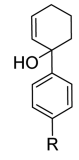
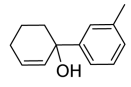
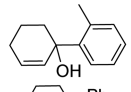
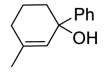
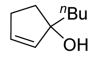
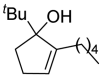
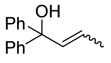
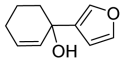
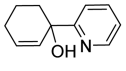
To achieve the proposed reaction for a one-pot synthesis of β-disubstituted α,β-unsaturated ketones from their corresponding allylic alcohols, we then began to investigate Pd-catalyzed aerobic oxidative reaction of the resultant allylic alcohols under the isomerization conditions.

We found out that this type of one-pot reaction could be realized by addition of $Pd(TFA)_2$, neocuproine, and $LiOH\cdot H_2O$ to the existing solution of the Pd-catalyzed 1,3-isomerization (Table 3). The reactions were performed at 80 °C for 20 h, and we can make the following observations: (1) six- and seven-membered-ring based substrates gave the corresponding β-disubstituted α,β-unsaturated ketones in good to excellent yields (Table 3, entries 1−13). (2) For

Table 2. Scope and Limitations of Catalytic 1,3-Isomerization[a]



1 2

entry	R	substrate	temp (°C)	product	yield (%)[b]
1	**1b** (^{s}Bu)		40	**2b**	93
2	**1c** (^{t}Bu)		40	**2c**	95
3	**1d** (Ph)		40	**2d**	90
4	**1e**		40	**2e**	93
5	**1f** (Me)		40	**2f**	91
6	**1g** (OMe)		40	**2g**	85
7	**1h** (CF_3)		40	**2h**	85
8	**1i** ($CH=CH_2$)		40	**2i**	87
9	**1j**		40	**2j**	90
10	**1k**		40	**2k**	91
11	**1l**		40	**2l**	75
12[c]	**1m**		0	**2m**	82
13[c]	**1n**		0	**2n**	55
14	**1o** (Ph)		40	**2o**	90
15	**1p**(^{n}Bu)		40	**2p**	81
16[d]	**1q**		80	**2q**	91
17[d]	**1r**		80	**2r**	89
18[d]	**1s**		80	**2s**	54
19[e]	**1t**		0	**2t**	94
20	**1u**		40	**2u**	0[f]

[a]Reaction conditions: substrate (1.0 mmol), $Pd(TFA)_2$ (0.2 mol %) in CH_3CN (5 mL), and H_2O (1 mL). [b]Isolated yields. [c]Reactions were carried out for 1 h. [d]$Pd(TFA)_2$ (0.4 mol %) was used. [e]Reactions were carried out for 0.5 h. [f]The starting material **1u** was recoverd.

acyclic allylic alcohol **1q**, conditions B were employed to realize the rearrangement step, and enone **3q** was isolated in 69% yield with 24% of starting material recovered (entry 14) (see the Supporting Information).

To ascertain the effect of $Pd(TFA)_2$ on the 1,3-isomerization of allylic alcohols, we conducted control experiments with substrate **1a** (Scheme 1). No isomerization was observed when substrate **1a** was stirred under the same conditions listed in Table 2 in the absence of $Pd(TFA)_2$, indicating $Pd(TFA)_2$ was essential to the 1,3-isomerization of allylic alcohols. Methyl

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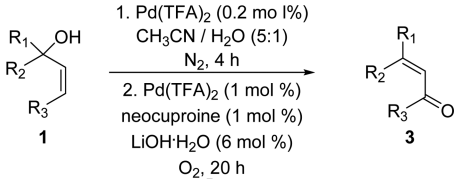
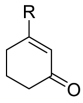
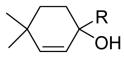
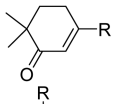
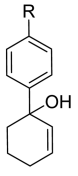
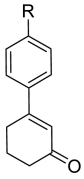
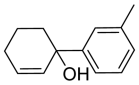
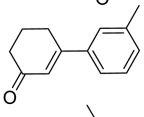
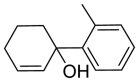
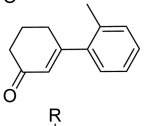
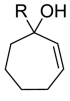
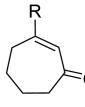
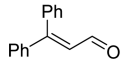
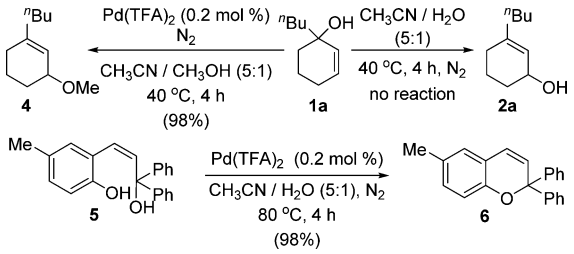
Table 3. One-Pot Oxidative Reactions of Allylic Alcohols[a]



entry	R	substrate	conditions	product	yield (%)[b]
1	**1a** (^{n}Bu)		A	**3a** 	81
2	**1b** (^{s}Bu)		A	**3b**	91
3	**1c** (^{t}Bu)		A	**3c**	92
4	**1d** (Ph)		A	**3d**	69
5	**1e** (Ph)		A	**3e** 	90
6	**1v**(^{n}Bu)		A	**3v**	79
7	**1f** (Me)		A	**3f** 	89
8	**1h** (CF_3)		A	**3h**	85
9	**1i** ($CH=CH_2$)		A	**3i**	66
10	**1j**		A	**3j** 	90
11	**1k**		A	**3k** 	91
12	**1o**(Ph)		A	**3o** 	58
13	**1p**(^{n}Bu)		A	**3p**	80
14	**1q**		B	**3q** 	69

[a]Conditions A: substrate (1.0 mmol), $Pd(TFA)_2$ (0.2 mol %) at 40 °C for 4 h; then $Pd(TFA)_2$ (1 mol %), neocuproine (1 mol %), LiOH·H_2O (6 mol %) at 80 °C for 20 h under an O_2 balloon. Conditions B: substrate (1 mmol), $Pd(TFA)_2$ (0.2 mol %) at 80 °C for 4 h; then $Pd(TFA)_2$ (1 mol %), neocuproine (1 mol %), and LiOH·H_2O (6 mol %) at 80 °C for 20 h under an O_2 balloon. [b]Isolated yields.

Scheme 1. Syntheses of Compounds 2a, 4, and 6



ether **4** was formed in almost quantitative yield when the 1,3-isomerization of allylic alcohol **1a** was carried out in the presence of $Pd(TFA)_2$ in the mixed solvents of CH_3CN/MeOH (5:1), indicating a similar π-allyl cation intermediate might be generated in this reaction.[15c,16b,20] Furthermore, when substrate **5** was utilized as the substrate, the intramolecular annulated product **6** was formed in 98% yield.

A proposed reaction mechanism is depicted in Figure 2. The key to direct conversion of allylic alcohol is the C−O bond cleavage giving delocalized carbocation intermediate **H**, which

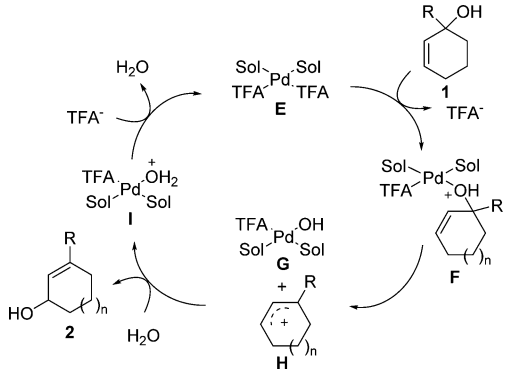


Figure 2. Proposed catalytic cycle of 1,3-isomerization of allylic alcohol catalyzed by $Pd(TFA)_2$.

followed by nucleophilic addition to afford product and regenerate catalyst. The regiochemistry of this reaction is governed by the stability of product. This mechanism is similar to that proposed by McCubbin and Hall.[15c,16b,20]

In summary, we have developed an efficient one-pot reaction of Pd catalysis for the conversion of tertiary allylic alcohols into their corresponding enals or enones. The reaction proceeds via the Pd-catalyzed isomerization of tertiary allylic alcohols followed by Pd-catalyzed aerobic oxidation. Overall, the study has been carried out in a reasonably divergent fashion that shows the scope and applicability.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedure, ^1H and ^{13}C NMR spectra, and X-ray data information. 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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