

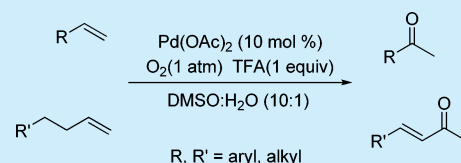
Wacker-Type Oxidation and Dehydrogenation of Terminal Olefins Using Molecular Oxygen as the Sole Oxidant without Adding Ligand

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Supporting Information

ABSTRACT: An efficient and economical palladium-catalyzed oxidation system has been identified. The oxidation system, characterized by not adding ligand and using molecular oxygen as the sole oxidant, can realize the Tsuji–Wacker oxidation of terminal olefins and especially styrenes to methyl ketones; in addition, this system can achieve tandem Wacker oxidation–dehydrogenation of terminal olefins to α,β -unsaturated ketones.



The palladium(II)-catalyzed oxidation of terminal olefins to methyl ketones, known as the Tsuji–Wacker oxidation, is one of the most important reactions that has extensive synthetic applications in laboratories and industries.^{1–4} Classically, the reaction is conducted with catalytic PdCl_2 and stoichiometric CuCl under aerobic atmosphere. Palladium decomposition,^{1b} olefin isomerization,^{2c,5} chlorinated byproducts,^{1b} and copper waste have been recognized as considerable limitations for oxidation.⁶ To address these limitations, many ligands of palladium have been developed,^{2d,7} and many oxidants, such as nitrous oxide,⁸ H_2O_2 ,⁹ 1,4-benzoquinone (BQ),¹⁰ pressurized oxygen,¹¹ and *tert*-butyl hydroperoxide (TBHP),^{7c,12} have been used. These modified methods undoubtedly widen the range of application of the Tsuji–Wacker oxidation. However, they also increase the cost of the oxidation and demand higher practical operation skills for the oxidation. Therefore, it is still highly desirable to develop a facile and efficient Wacker-type oxidation that does not rely on the ligand and uses ambient-pressure oxygen as the sole oxidant.

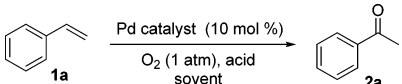
Acetophenones, as valuable intermediates for the manufacture of a variety of pharmaceuticals, perfumes, resins, pesticides and other chemical products, can be reasonably obtained from styrenes by Tsuji–Wacker oxidation.¹³ Nevertheless, styrenes are problematic substrates for the reaction due to facile polymerization and oxidative cleavage to benzaldehydes and/or benzoic acids.¹⁴ In general, molecular oxygen can be applied for the Tsuji–Wacker oxidation of alkyl-substituted terminal olefins,^{7d} while a stronger oxidant, such as TBHP, is required for such oxidation of styrenes.^{12b,15} A breakthrough was obtained by Reiser et al. in 2010, who employed chiral pseudo-C₂-symmetrical bis(isonitrile) as ligand to realize palladium-catalyzed Tsuji–Wacker oxidation of styrenes using molecular oxygen as oxidant. Herein, we report a palladium(II)-catalyzed Tsuji–Wacker oxidation of olefins and especially styrenes to methyl ketones using ambient-pressure oxygen as the sole oxidant without introducing any extra ligand.

Since styrenes are valuable but challenging substrates for Tsuji–Wacker oxidation, we first chose them to study the reaction. In preliminary experiments, styrene was treated with 10 mol % of Pd(OAc)_2 and trifluoroacetic acid (TFA, 8 equiv) in $\text{DMSO/H}_2\text{O}$ (10:1) under an oxygen atmosphere (O_2 balloon) at room temperature for 24 h. We found the conversion of the reaction was low (<30%) (Table 1, entry 1). Increasing the temperature could greatly improve the reaction rate, but higher temperature led to a significant drop in the yield due to the decomposition of starting material and product (entries 2–4). Changing the solvent did not enhance reactivity (entry 5). By investigating the amount of TFA, we found that 1 equiv of TFA was the optimal amount to afford the desired product in 86% yield, and in the absence of trifluoroacetic acid, the reaction would proceed with much low conversion (entries 6–9). Using other palladium sources and acids, the yield of acetophenone could not be improved (entries 10–14). When air was used as oxidant instead of oxygen, the reaction rate and the yield obviously dropped (entry 15). When the loading of Pd(OAc)_2 was lowered, e.g., to 5 mol %, the reaction was slow and would proceed incompletely (entry 16). Accordingly, the reaction conditions were optimized as follows: Pd(OAc)_2 (10 mol %), TFA (1 equiv) under oxygen atmosphere in $\text{DMSO/H}_2\text{O}$ (10:1) at 70 °C.

After identifying the optimized conditions, we examined the scope of styrenes (Table 2). We were pleased with the generality of this method. Styrenes possessing either electron-withdrawing groups or electron-donating groups were found to smoothly react and provided acetophenones in good to excellent yields (76–95%, entries 1–8). The position of the substituted group on the phenyl ring almost did not affect the reactivity (entries 4–6). Sterically hindered 2,4,6-trimethylstyrene also readily converted into 2,4,6-trimethylacetophenone in 76% yield (entry 9). In all cases, the reaction was of complete

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Table 1. Optimization of Reaction Conditions^a


entry	cat.	acid (equiv)	temp (°C)	time (h)	yield ^f (%)
1	Pd(OAc) ₂	TFA (8)	rt	24	25
2	Pd(OAc) ₂	TFA (8)	50	12	66
3	Pd(OAc) ₂	TFA (8)	70	12	74
4	Pd(OAc) ₂	TFA (8)	90	12	54
5 ^b	Pd(OAc) ₂	TFA (8)	70	12	<56
6	Pd(OAc) ₂	TFA (5)	70	12	81
7	Pd(OAc) ₂	TFA (1)	70	12	86
8	Pd(OAc) ₂	TFA (0.5)	70	12	77
9 ^c	Pd(OAc) ₂		70	12	<10
10	Pd(TFA) ₂	TFA (1)	70	12	79
11	PdCl ₂	TFA (1)	70	12	nd
12	Pd(OH) ₂	TFA (1)	70	12	30
13	Pd(PPh ₃) ₂ Cl ₂	TFA (1)	70	12	nd
14 ^d	Pd(OAc) ₂	Acids (1)	70	12	<45
15 ^e	Pd(OAc) ₂	TFA (1)	70	24	57
16 ^g	Pd(OAc) ₂	TFA (1)	70	24	48 ^h

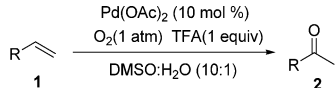
^aReaction conditions: **1a** (1 mmol), catalyst (0.1 mmol), O₂ (1 atm), and acid in DMSO/H₂O (10:1, 5 mL) at the specified temperature.

^bSolvents used instead of DMSO: EtOAc, DMF, THF, *n*-hexane, toluene, acetone, CH₃CN, dioxane, Et₂O, CH₂Cl₂, CHCl₃, CH₃NO₂, EtOH. ^cNo acid. ^dHCO₂H, AcOH, PhCO₂H, tartaric acid, *p*-toluenesulfonic, salicylic acid, boric acid, oxalic acid, maleic acid, fumaric acid. ^eUsing air as oxidant. ^fIsolated yield. ^gPd(OAc)₂ (5 mol %) was used. ^hThe conversion was 52%.

Markonikov selectivity, and no benzaldehydes or polymeric products could be detected by analyzing the reaction mixtures. Aliphatic terminal olefins were also compatible with the reaction to provide the products in good yields and complete Markonikov selectivity (entries 10–14). In addition, under the standard reaction conditions, the reaction of aliphatic olefins was obviously faster than that of styrenes.

To our surprise, when 4-phenyl-1-butene was used as substrate, we attained a sole product, *trans*-4-phenyl-3-buten-2-one in 87% yield (Scheme 1). This means that the Pd(OAc)₂–TFA oxidative system has more potential to realize deeper oxidation of the products to generate α,β -unsaturated ketones. It is well-known that α,β -unsaturated ketones are versatile synthetic intermediates that are frequently prepared via multistep routes,¹⁶ for instance, α -bromination–dehydrobromination,¹⁷ sulfoxide or selenoxide elimination,¹⁸ Saegisa oxidation,¹⁹ etc. In 2012, Zhao et al. and Stahl et al., respectively, reported Pd(II)-catalyzed aerobic dehydrogenations of carbonyl compounds to form corresponding α,β -unsaturated carbonyl compounds.²⁰ In the two studies, the same ligand of palladium, 4,5-diazafluorenone, was exploited. More recently, White et al. reported an elegant tandem Wacker oxidation–dehydrogenation to generate α,β -unsaturated ketones directly from terminal olefins.²¹ In the approach, they used Pd(CH₃CN)₄(BF₄)₂ (10 mol %) and PhI(OAc)₂ (25 mol %) as cocatalyst and 1,4-benzoquinone (2 equiv) as oxidant.

Inspired by this research and our above findings, we intended to develop a palladium-catalyzed tandem Wacker oxidation–dehydrogenation of terminal olefins using molecular oxygen as the sole oxidant and without the need of extra ligand. To our delight, the Pd(OAc)₂–TFA oxidative system was indeed able to accomplish the conversion (Table 3). 4-Aryl-1-butenes,

Table 2. Substrate Scope of the Palladium-Catalyzed Wacker Oxidant Reaction^a


entry	alkene	product	time (h)	yield (%) ^b
1 ^c	1a	2a	12	86
2	1b	2b	10	94
3	1c	2c	10	92
4	1d	2d	10	88
5	1e	2e	10	85
6	1f	2f	10	95
7	1g	2g	10	86
8	1h	2h	10	91
9	1i	2i	10	76
10	1j	2j	8	69
11	1k	2k	6	89
12	1l	2l	6	83
13	1m	2m	8	78
14 ^d	1n	2n	8	81

^aReaction conditions: alkene (1 mmol), Pd(OAc)₂ (0.1 mmol), O₂ (1 atm) and TFA (1 mmol) in DMSO/H₂O (10:1, 5 mL) at 70 °C.

^bIsolated yield. ^c10 mmol of styrene was used. ^dAt 100 °C.

bearing an electron-withdrawing or electron-donating substituent on aromatic ring, all smoothly underwent tandem Wacker oxidation–dehydrogenation to deliver the desired α,β -

Scheme 1. Palladium-Catalyzed Tandem Wacker Oxidation–Dehydrogenation of 4-Phenyl-1-butene

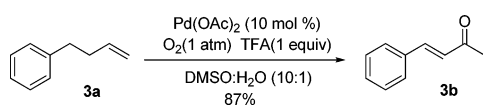


Table 3. Substrate Scope of the Reaction of Terminal Olefins to α,β -Unsaturated Ketones^a

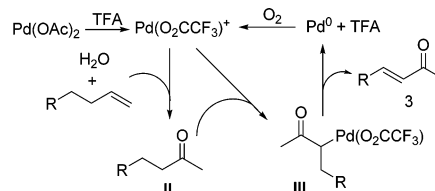
entry	alkene	product	time (h)	yield (%) ^b
1			10	87 (92 ^c)
2 ^d			8	72
3			8	74
4			8	77
5 ^d			8	77
6			8	75
7 ^e			8	53
8 ^e			8	55

^aReaction conditions: alkene (1 mmol), Pd(OAc)₂ (0.1 mmol), O₂ (1 atm), and TFA (1 mmol) in DMSO/H₂O (10:1, 5 mL) at 70 °C. ^bIsolated yield. ^cYield in parentheses was obtained with 10 mmol of 4-phenyl-1-butene. ^dAt 100 °C. ^eTFA (0.5 mmol) was used; piperidine (0.1 mmol) was added.

unsaturated ketones in good yields (70–87%) (entries 1–6). A number of important functional groups are tolerated under the reaction conditions, such as alkyl, MeO, F, and CF₃. We further investigated tandem Wacker oxidation–dehydrogenation of 4-alkyl-1-butenes and were pleased to obtain the corresponding α,β -unsaturated carbonyl products under slightly altered reaction conditions in which a catalytic amount of piperidine was employed (entries 7 and 8). In addition, the reaction can be conducted on a gram scale (1.32 g, 10 mmol) in a slightly enhanced yield (Table 3, entry 1).

Our current understanding of the mechanism of the reaction is shown in Scheme 2. Pd(OAc)₂ is treated with TFA to obtain active Pd(O₂CCF₃)⁺,²² which converts olefin into the methyl ketone (II) by Wacker oxidation.²³ The ketone (II) undergoes

Scheme 2. Plausible Mechanism of the Reaction



the formation of palladium enolate followed by β -hydride elimination to afford the α,β -unsaturated ketone,^{20,24} and the Pd⁰ can be reoxidized to Pd(O₂CCF₃)⁺ by O₂ in the presence of TFA to complete the catalytic cycle.²⁵

In summary, we have identified a simple, efficient, and economical Pd(II)-catalyzed ligandless oxidation system using molecular oxygen as the sole oxidant at ambient pressure. The catalytic system can oxidize terminal olefins and especially styrenes to methyl ketones. The reaction is of complete Markonikov selectivity, and no aldehydes or polymeric products can be detected. The catalytic system can also facilitate tandem Wacker oxidation–dehydrogenation to generate α,β -unsaturated ketones directly from terminal olefins. The method should have many applications in synthetic chemistry. Studies of the detailed mechanism and applications of this catalytic system are in progress.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures including spectroscopic and analytical 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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