

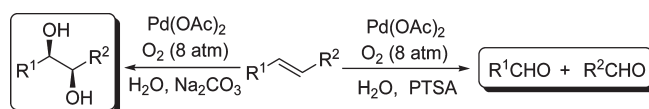
Palladium-Catalyzed Direct Oxidation of Alkenes with Molecular Oxygen: General and Practical Methods for the Preparation of 1,2-Diols, Aldehydes, and Ketones

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1,2-Diols, aldehydes, and ketones are important intermediates in chemical synthesis, and alkenes are possible precursors for 1,2-diols, aldehydes, and ketones. Herein, novel and environmentally benign methods for palladium-catalyzed dihydroxylation and oxidative cleavage of olefins with oxygen as sole oxidant are presented. The cleavage reactions were performed with acid as additive in aqueous solution, whereas 1,2-diols were formed in the presence of base. A broad substrate scope has been demonstrated allowing monosubstituted aromatic and aliphatic terminal alkenes, 1,2-disubstituted, and 1,1-disubstituted olefins. The cleavage reactions of dioxo-Pd^{II} complexes implicate 1,2-diol might act as a key intermediate of olefin cleavage.

Introduction

Alkene oxidation reactions are of fundamental importance in organic synthesis.¹ For example, *cis*-dihydroxylation and oxidative cleavage of olefins are highly versatile synthetic methods for the preparation of valuable intermediates.² Over the past several decades, many research groups have focused their interest on the development of efficient and active catalytic systems for alkene *cis*-dihydroxylation and cleavage. The *cis*-dihydroxylation of alkenes by osmium tetroxide has long been

known (Scheme 1).³ In recent years, transition metal catalysts such as ruthenium,⁴ iron,⁵ manganese,⁶ cobalt,⁷ or molybdenum⁸ have been used to convert olefins into *cis*-1,2-diols.

Oxidative alkene cleavage reactions are classically carried out by ozonolysis;⁹ however, their utility is often limited by safety concerns. This transformation can be performed also catalytically with high-valent oxometals such as RuO₄ and OsO₄.¹⁰ Very recently, aryl-λ³-iodane-based methods for C–C double bond cleavage have been reported.¹¹ Despite great progress having been made in the field of alkene *cis*-dihydroxylation and oxidative cleavage, processes based on expensive and “nongreen”

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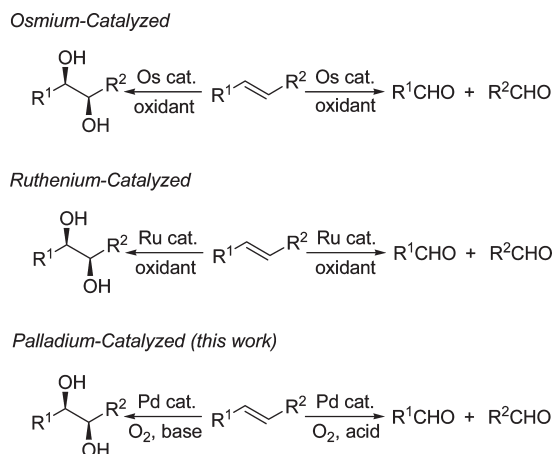
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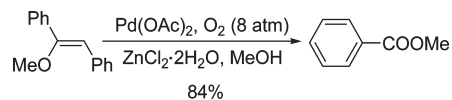
SCHEME 1. Progression of Strategies for Dihydroxylation and Oxidative Cleavage of Olefins


oxidants are still used extensively.¹² Therefore, the development of alternative protocols for alkene dihydroxylation and cleavage that would be cleaner and amenable to large-scale synthesis would constitute a breakthrough in both green chemistry and organic synthesis.

On the other hand, the utilization of molecular oxygen as oxidant is one of the most important goals in oxidation chemistry.¹³ Palladium-catalyzed aerobic oxidation reactions have been shown to be highly versatile in preparing fine chemicals.¹⁴ In particular, the development of the Wacker process in the late 1950s had a significant impact on the chemical industry.¹⁵ Herein, we report an efficient oxidation of a wide range of olefins to 1,2-diols, aldehydes, or ketones catalyzed by palladium with O₂ as the sole oxidant. These reactions constitute an economically attractive and environmentally friendly synthesis of 1,2-diols and carbonyl compounds and may be suitable for large-scale operations.

Results and Discussion

Palladium-Catalyzed Oxidative Cleavage of Alkenes with Oxygen. In 2008, we disclosed a Lewis acid-promoted and palladium-catalyzed oxidative cleavage of a carbon–carbon triple bond with O₂ in which alkyne is split into carboxylic ester in alcohols.¹⁶ As a starting point for this work, we observed

SCHEME 2. Palladium-Catalyzed Oxidative Cleavage of 1-Methoxy-1,2-diphenylethene in MeOH

TABLE 1. Optimization of Reaction Conditions for the Palladium-Catalyzed Oxidative Cleavage of *trans*-Stilbene^a

entry	Pd cat.	additive	solvent	yield (%) ^b
1	Pd(OAc) ₂	ZnCl ₂	MeOH	trace
2	Pd(OAc) ₂		MeOH	36
3	Pd(OAc) ₂		DMSO	trace
4	Pd(OAc) ₂		DMF	trace
5	Pd(OAc) ₂		toluene	35
6	Pd(OAc) ₂		<i>t</i> -BuOH	38
7	Pd(OAc) ₂		H ₂ O	43
8	Pd(OAc) ₂	CH ₃ COOH	H ₂ O	79
9	Pd(OAc) ₂	PTSA	H ₂ O	88 (85)
10	Pd(OAc) ₂	CH ₃ SO ₃ H	H ₂ O	81
11	Pd(OAc) ₂	CF ₃ COOH	H ₂ O	77
12	PdCl ₂	PTSA	H ₂ O	14
13	Pd ₂ dba ₃	PTSA	H ₂ O	trace
14	PdI ₂	PTSA	H ₂ O	16
15	Pd(NO ₃) ₂	PTSA	H ₂ O	21
16	Pd/C	PTSA	H ₂ O	8
17		PTSA	H ₂ O	0

^aReaction conditions: All reactions were performed with **1a** (1 mmol), pressure of O₂ (8 atm), Pd catalyst (2 mol %), and additive (20 mol %) in 3 mL of solvent for 24 h, 100 °C. ^bDetermined by GC analysis of crude reaction mixture with naphthalene as an internal standard; the number in parentheses is the yield of isolated product based on complete alkene consumption.

in control experiments that the cleavage reaction of 1-methoxy-1,2-diphenylethene in MeOH afforded methyl benzoate (Scheme 2).¹⁶ This has encouraged us to explore the oxidative cleavage reactions of olefins. We examined the cleavage reaction of *trans*-stilbene under different reaction conditions, and the results are summarized in Table 1. As expected, a combination of Pd(OAc)₂ with ZnCl₂ in MeOH, the most effective system for the cleavage reaction of alkynes, led to the formation of methyl benzoate with a trace of benzaldehyde (Table 1, entry 1). With the goal of optimizing the reaction for the formation of benzaldehyde, ZnCl₂ was removed and the desired product was obtained in 36% GC yield (Table 1, entry 2).

Subsequently, a series of other solvents were evaluated, and H₂O provided the best result (Table 1, entries 2–7). It is worth mentioning that the use of water as solvent is more advantageous than the use of organic solvent for environmental considerations. Further exploration revealed that the yield could be improved when a Brønsted acid was utilized as the additive in the reaction.¹⁷ Among the Brønsted acids investigated, PTSA (*p*-toluenesulfonic acid monohydrate) was the best choice (Table 1, entries 8–11). Different palladium species were also tested, such as PdCl₂, Pd₂dba₃, PdI₂,

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Pd(NO₃)₂, and Pd/C, but the reaction did not proceed well (Table 1, entry 8 vs entries 12–16). Moreover, the reaction without Pd(OAc)₂ did not give the desired product at all, and **1a** was recovered quantitatively (entry 17).

The optimized conditions are applicable to the oxidative cleavage reaction of other alkenes (Table 2). Styrene and 2-vinylnaphthalene were easily converted to benzaldehyde and 2-naphthaldehyde in high yields (Table 2, entries 1 and 2). Other aromatic terminal alkenes with electron-rich and electron-poor substituents in the para position reacted to give the corresponding aldehydes in high yields (81–89%, Table 1, entries 3–7), while meta-substituted aromatic terminal alkenes afforded only moderate yields of the desired products (Table 2, entries 8 and 9). 1,2-Disubstituted olefins were also subjected to the oxidative cleavage. *cis*-Stilbene and *trans*- β -methylstyrene provided benzaldehyde in 86% and 84% yields, respectively (Table 2, entries 10 and 11). α,β -Unsaturated alkenes, including *trans*-methyl cinnamate, *trans*-methyl 3-(thiophen-2-yl)acrylate, and *trans*-methyl 3-(furan-3-yl)acrylate, produced the corresponding aldehydes in 76%, 67%, and 69% isolated yields, respectively (Table 2, entries 12–14). The oxidation of 1,1-disubstituted olefins occurred efficiently to give the ketones in high yields (Table 2, entries 15–18). Yet, the oxidative cleavage of tetra-substituted olefins such as 1,1,2,2-tetraphenylethene appeared to be less effective, and the corresponding benzophenone was obtained in only 23% yield (Table 2, entry 19). The linear aliphatic alkenes were also converted to the corresponding aldehydes efficiently (Table 2, entries 20 and 21).

Palladium-Catalyzed Dihydroxylation of Alkenes with Oxygen. In our experiment of optimization of reaction conditions for alkene cleavage, 1,2-diol was detected when the reaction was carried out in H₂O without any additives (Table 1, entry 7). Because 1,2-diols are valuable intermediates for the perfume and cosmetic industry, for the preparation of pharmaceuticals, agrochemicals, and fine chemicals,¹⁸ we tried to apply the Pd(OAc)₂/O₂ system in alkene dihydroxylation. The dihydroxylation of styrene was used as a test reaction. The oxidation shows high conversion but undesired selectivity for the aldehyde without adding any additives (Table 3, entry 1). Considering the presence of base may assist the hydrolysis process,¹⁹ a variety of bases were examined wherein it was found that the use of Na₂CO₃ gives the best yield of the reaction and selectivity for 1,2-diol (Table 3, entries 2–8). The lowering of the reaction temperature had a detrimental effect on the dihydroxylation, and a small amount of acetophenone was also formed along with the desired product (Table 3, entry 9).

To extend the scope of this methodology to the synthesis of 1,2-diols, various alkenes were reacted under the optimized reaction conditions. In almost all the cases tested, the dihydroxylation went smoothly, giving a good yield of the desired products. As shown in Table 4, aromatic terminal olefins afforded the corresponding products in 74–87% yields (Table 4, entries 1–5), and the aliphatic terminal olefins were also applicable (Table 4, entries 6–8). Importantly, the 1,2-disubstituted olefins could be converted selectively to the corresponding *cis*-1,2-diols in reasonable to good yields

TABLE 2. Substrate Scope of the Palladium-Catalyzed Alkene Cleavage Reaction^a

entry	alkene	product	yield (%) ^b
1	2a	1b	88
2	3a	2b	88
3	4a	3b	84
4	5a	4b	86
5	6a	5b	89
6	7a	6b	83
7	8a	7b	81
8	9a	8b	53
9	10a	9b	61
10	11a	1b	86
11	12a	1b	84
12	13a	1b	76
13	14a	10b	67
14	15a	11b	69
15 ^c	16a	12b	85
16 ^c	17a	13b	84
17 ^c	18a	14b	87
18 ^c	19a	15b	84
19 ^c	20a	14b	23
20	21a	16b	74
21	22a	16b	68

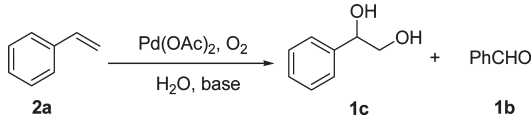
^aReaction conditions: alkene (1 mmol), Pd(OAc)₂ (2 mol %), pressure of O₂ (8 atm), H₂O (3 mL), PTSA (20 mol %), 100 °C, 24 h. ^bYield of isolated product based on complete alkene consumption. ^cH₂O/ClCH₂CH₂Cl (2:1 v/v).

(Table 4, entries 9–12). Moreover, this transformation could be successfully extended to a variety of 1,1-disubstituted olefins (Table 4, entries 13–16). It is noteworthy that product **16c** is a key intermediate for triazole antifungal agents.²⁰

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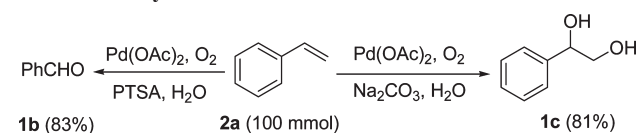
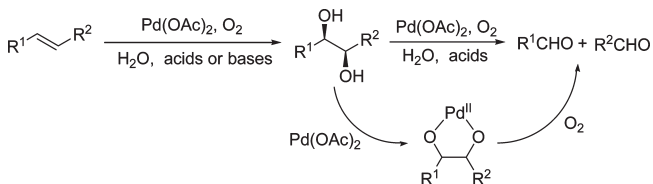
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TABLE 3. Optimization of Reaction Conditions for the Palladium-Catalyzed Dihydroxylation of Styrene^a


entry	base	temp (°C)	conv (%) ^b	yield of 1c (%) ^b	1c:1b
1		100	96	6	7:93
2	NaOAc	100	95	13	13:87
3	KOAc	100	95	14	16:84
4	CsOAc	100	91	43	49:51
5	NaOH	100	trace		
6	Na ₂ CO ₃	100	91	84 (83)	93:7
7	K ₂ CO ₃	100	89	79	96:4
8	Cs ₂ CO ₃	100	trace		
9	Na ₂ CO ₃	80	56	37	92:8

^aUnless otherwise indicated, all reactions were performed with styrene (1 mmol), Pd(OAc)₂ (4 mol %), and base (2 mmol) in 3 mL of H₂O for 24 h. ^bDetermined by GC analysis of crude reaction mixture with naphthalene as an internal standard; the number in parentheses is the yield of isolated product based on complete alkene consumption.

SCHEME 3. Large-Scale Synthesis of 1-Phenylethane-1,2-diol and Benzaldehyde**SCHEME 4. Possible Pathway of the Alkene Cleavage**

To highlight the utility of these reactions, the dihydroxylation and oxidative cleavage reaction of styrene were successfully scaled to 100 mmol, the isolated yields (based on complete alkene consumption) of these reactions remain at 81% and 83%, respectively (Scheme 3).

Palladium-Catalyzed Oxidative Cleavage of 1,2-Diols. Why is it that the 1,2-diols are formed under alkaline conditions whereas the C–C double bond was cleaved in the presence of acid? We speculated that the palladium-catalyzed dihydroxylation protocol was accompanied by overoxidation when acid was employed in the reaction. To test this hypothesis, we treated *trans*-1,2-diphenylethane-1,2-diol (**10c**) with 0.2 equiv of PTSA in the presence of 2 mol % of Pd(OAc)₂ under 8 atm of O₂ in water at 100 °C for 24 h. To our delight, 94% isolated yield of benzaldehyde was obtained (Table 5, entry 1). The cleavage reaction of **10c** gave benzaldehyde in 46% yield without adding any additives (Table 5, entry 2). However, only a trace of cleavage product was observed under alkaline conditions (Table 5, entry 3). Besides, the reaction provided no conversion without palladium catalyst. Next, several other 1,2-diols were also investigated in the reaction, and in all cases, the desired products were formed in high yields under acidic conditions

TABLE 4. Substrate Scope of the Palladium-Catalyzed Alkene Dihydroxylation^a

entry	alkene	product	yield (%) ^b
1			85
2			83
3			74
4			87
5			78
6			71
7			82
8			79
9			76
10			75
11			66
12			58
13			72
14			74
15			57
16			51






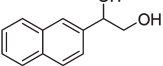
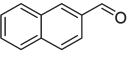
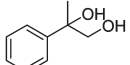
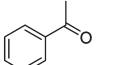
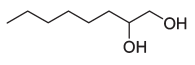
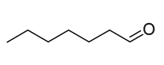
^aUnless otherwise indicated, reactions were carried out with 1.0 mmol of alkene, 4 mol % of Pd(OAc)₂, 2 mmol of Na₂CO₃, 8 atm of O₂, and 3 mL of H₂O, at 100 °C for 24 h. ^bThe yield of isolated product is based on complete alkene consumption.

(Table 5, entries 5–8). Accordingly, a possible pathway was proposed for the aldehydes formation (Scheme 4): 1,2-diol is formed and then transformed into the dioxo–Pd^{II} intermediate, which undergoes C–C bond cleavage to produce aldehydes under oxygen atmosphere.

In an attempt to rationalize the possible pathway, two dioxo–Pd^{II} complexes (Figure 1), (1,10-phenanthroline)(1,2-octanediolato)Pd^{II} **A** and (1,10-phenanthroline)(1,2-ethanediolato)Pd^{II} **B** were prepared.²¹ Dioxo–Pd^{II} complexes **A** and

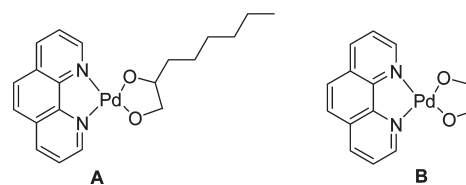
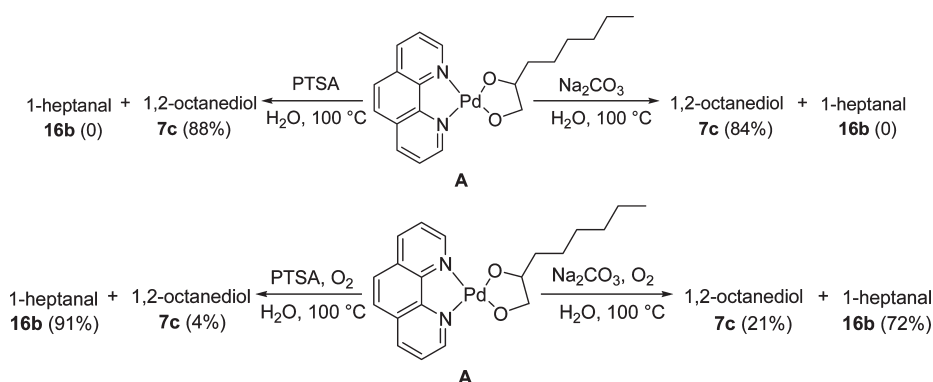
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TABLE 5. Palladium-Catalyzed Oxidative Cleavage of 1,2-Diols^a

entry	1,2-diol	product	yield (%) ^b
1		PhCHO	94
2 ^c		PhCHO	46
3 ^d		PhCHO	<3
4 ^e		-	-
5		PhCHO	95
6			93
7			96
8			89

^aUnless otherwise indicated, reactions were carried out with 1.0 mmol of 1,2-diol, 2 mol % of Pd(OAc)₂, 0.2 mmol of PTSA, 8 atm of O₂, and 3 mL of H₂O, at 100 °C for 24 h. ^bThe yield of isolated product is based on complete alkene consumption. ^cThe reaction was carried out without any additives. ^dThe reaction was carried out with 2 mmol of Na₂CO₃ as additive. ^eIn the absence of Pd catalysts.

B were quite stable in refluxing toluene under nitrogen atmosphere and no product was detected by GC analysis. Only 17% GC yield of 1,2-octanediol was obtained when placing complex **A** in boiling water. Treatment of complex **A** (1 mmol) with PTSA (0.2 mmol) in water at 100 °C produced 1,2-octanediol in 88% isolated yield without any 1-heptanal being detected (Scheme 5). Changing PTSA to Na₂CO₃ (2 mmol) had no significant impact on the product, 1,2-octanediol was obtained in 84% yield. These results suggest that acid and base promote the hydrolysis of dioxo-Pd^{II} complexes. To gain the cleavage product of dioxo-Pd^{II} complex **A**, several oxidants [CuCl₂, Cu(OAc)₂, benzoquinone, and O₂] were employed in the reaction. It was found that CuCl₂, Cu(OAc)₂, and benzoquinone

SCHEME 5. Hydrolysis and Cleavage Reaction of Dioxo-Pd^{II} Complexes **A****FIGURE 1.** Dioxo-Pd^{II} Complexes.

had no effect on the cleavage reaction. The employment of O₂ as oxidant is critical for the aldehyde formation. When the reaction of complex **G** with PTSA was undertaken in 8 atm of O₂, 1-heptanal was obtained in 91% yield. Changing PTSA to Na₂CO₃ afforded 1-heptanal in 72% yield along with 1,2-octanediol (21%). These experiments show that 1,2-diols or dioxo-Pd^{II} complexes might be the precursors for the formation of carbonyl compounds and O₂ plays an important role in these reactions.

Conclusions

In conclusion, we have developed an environmentally benign and general procedure for the palladium-catalyzed dihydroxylation and oxidative cleavage of olefins with O₂ as sole oxidant. Although at its early state of development these processes may lend themselves to large-scale applications, an important, but as yet unanswered, question is how acids and bases play an important role in these oxidations. This challenge will stimulate our further studies to disclose the nature of the present transformations. Our current research is focused on extending the scope and gaining more detailed information on the exact mechanism of these oxidations. Considering the high value of chiral vicinal diols, we anticipate that the asymmetric version of this dihydroxylation will be the subject of future research.

Experimental Section

General Procedure for Palladium-Catalyzed Oxidative Cleavage of Alkenes with O₂. The reactions were carried out in a HF-15 autoclave. Pd(OAc)₂ (4.49 mg, 0.02 mmol), PTSA (38 mg, 0.2 mmol), H₂O (3 mL), and alkene (1 mmol) were added into a 15 mL autoclave in sequence. O₂ was pumped into the autoclave with a cooling pump to reach the desired pressure, then the autoclave was heated with an oil bath under magnetic stirring for the desired reaction time. After the reaction was finished, the autoclave was allowed to cool to 0 °C. O₂ was vented, the surplus was extracted with EtOAc (30 mL), and the organic phase was washed with aq NaHCO₃. The organic layer was dried over

anhydrous Mg_2SO_4 and concentrated under reduced pressure to give crude product. The crude product was purified by chromatography on a silica gel column, using light petroleum ether/ethyl acetate as eluent.

General Procedure for Palladium-Catalyzed Dihydroxylation of Alkenes with O_2 . The reactions were carried out in a HF-15 autoclave. $\text{Pd}(\text{OAc})_2$ (8.98 mg, 0.04 mmol), Na_2CO_3 (212 mg, 2 mmol), H_2O (3 mL), and alkene (1 mmol) were added into a 15 mL autoclave in sequence. O_2 was pumped into the autoclave with a cooling pump to reach the desired pressure, then the autoclave was heated with an oil bath under magnetic stirring for the desired reaction time. After the reaction was finished, the autoclave was allowed to cool to 0 °C. O_2 was vented and the

surplus was extracted with EtOAc (30 mL). The organic layer was dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure to give crude product. The crude product was purified by chromatography on a silica gel column, using light petroleum ether/ethyl acetate as eluent.

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Supporting Information Available: Full experimental details and copies of NMR spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.