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Oxidative Esterification

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General and Selective Palladium-Catalyzed Oxidative Esterification of Alcohols**

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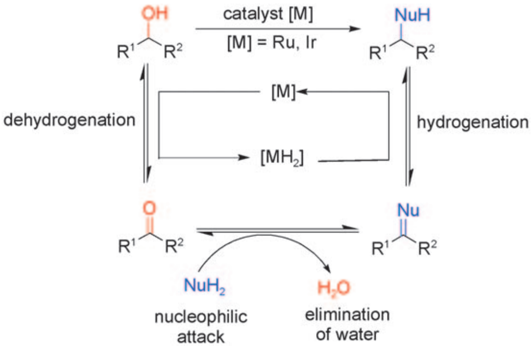
Dedicated to Professor Jae Nyoung Kim on the occasion of his 50th birthday

The development of new selective catalytic oxidations that apply molecular oxygen in organic synthesis remains a challenging task, which is of importance for chemical industry as well as academic research.[1] Apart from oxidations of olefins and alkynes, especially oxidative transformations of easily available alcohols are of interest in this context.

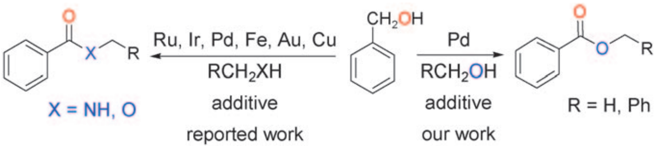
In recent years, cascade sequences that use dehydrogenation-functionalization reactions became a popular concept for the selective activation of alcohols (Scheme 1).[2] Such reactions have been named "hydrogen-borrowing methodology"[3] or "hydrogen autotransfer processes"[4]; they generate new C–C or C–N bonds with water as the only by-product.[5]



Scheme 1. Proposed mechanism for dehydrogenative activation of alcohols and subsequent functionalization.

However, so far relatively little work has been carried out on similar oxidative transformations. An important milestone in this context was the realization of oxidative esterifications of primary alcohols in the presence of ruthenium pincer complexes by Milstein and co-workers.[6] Later on, Williams and co-workers demonstrated the utility of [Ru$(PPh_3)_3(CO)H_2$]/xantphos for the catalytic synthesis of methyl esters from primary alcohols in the presence of crotonitrile as hydrogen acceptor.[7] Similarly, Grützmacher and co-workers observed oxidations to esters and carboxylic acids using a cationic rhodium catalyst in the presence of a hydrogen acceptor.[8] In addition, few iridium complexes are known to catalyze this type of reaction.[9,10] Unfortunately, in most cases stoichiometric amounts of organic by-products are formed.

Herein we report general catalytic oxidative cross-esterifications of benzylic and aliphatic alcohols, which proceed highly selectively under mild conditions with air as oxidant.[11] To the best of our knowledge, no similar palladium-catalyzed reactions are known to date (Scheme 2).



Scheme 2. Oxidative dimerization of alcohols to esters.

Our discovery is based on the recent development of novel palladium-catalyzed arylations of primary alcohols with aryl and heteroaryl halides.[12] While investigating the coupling of 2-bromotoluene with *n*-butanol, we observed the formation of *n*-butyl butyrate as side product depending on the palladium catalyst system. Obviously, in this case the corresponding aryl halide acted as the oxidation reagent that produced stoichiometric amounts of unwanted toluene as by-product.

Nevertheless, this transformation attracted our interest and we studied the palladium-catalyzed reaction of benzyl alcohol with and without methanol in the presence of air as oxidant in more detail. As shown in Table 1 (entries 1 and 2), in the presence of 2 mol% [Pd$(OAc)_2$] without any ligand only the well-known oxidation towards benzaldehyde occurred in fair yield.[13] Using methanol as solvent and adding K_2CO_3 as base led to some cross-esterification product (43% methyl benzoate). However, the reaction proceeded in a nonselective manner and the catalyst immediately turned black (Table 1, entries 3–4).

To improve the stability and chemoselectivity of the catalyst system, the influence of various ligands was inves-

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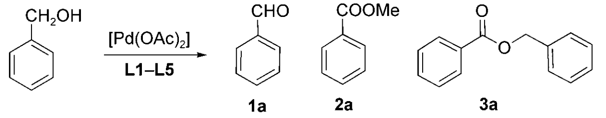
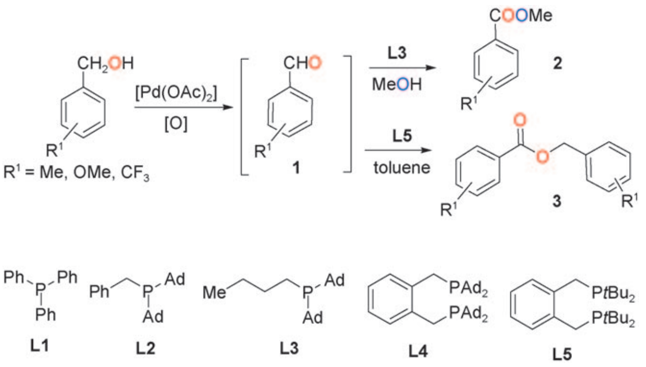
Table 1: Oxidative esterification of benzyl alcohol with and without methanol: Influence of Pd catalyst systems.



Entry	Additive	Ligand	Solvent[a,b]	Yield [%][d]		
				1a	**2a**	**3a**
1[e]	–	–	MeOH	2	–	–
2[e]			toluene	50	–	–
3	–	–	MeOH	10	43	–
4			toluene	62	–	–
5	$AgPF_6$	–	MeOH	14	65	–
6			toluene	49	–	–
7	$AgPF_6$	**L1**	MeOH	4	55	–
8			toluene	–	–	20
9	$AgPF_6$	**L2**	MeOH	5	46	–
10			toluene	4	–	33
11	$AgPF_6$	**L3**	MeOH	–	88	–
12			toluene[c]	84	–	–
13	$AgPF_6$	**L4**	MeOH	–	27	–
14			toluene	–	–	46
15	$AgPF_6$	**L5**	MeOH	5	5	–
16			toluene	–	–	85
17	$AgBF_4$	**L3**	MeOH	–	81	–
18		**L5**	toluene	10	–	69
19	$AgNO_3$	**L3**	MeOH	32	33	–
20		**L5**	toluene	20	–	35
21	Ag_2O	**L3**	MeOH	17	58	–
22		**L5**	toluene	25	–	40

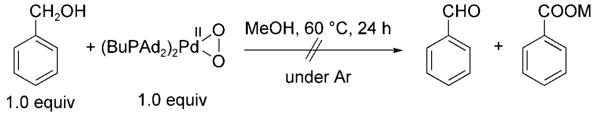
Reaction conditions: [a] Conditions a: 2 mol% $Pd(OAc)_2$, 4 mol% **L1**–**L5**, 4 mol% silver salt, 50 mol% K_2CO_3, 1 mL MeOH, 50–60 °C, 1 bar O_2. [b] Conditions b: 5 mol% $[Pd(OAc)_2]$, 5 mol% **L1**–**L5**, 5 mol% silver salt, 120 mol% K_2CO_3, 1 mL toluene, 90–100 °C, 1 bar O_2. [c] 5 mol% $[Pd(OAc)_2]$, 5 mol% **L3**, 30 mol% K_2CO_3, 1 mL toluene, 80 °C. [d] 18–20 h, GC yield. [e] No base was added.

tigated in more detail in the presence of different silver salts. From a study of more than 15 different ligands (Scheme 3; see also the Supporting Information) bulky mono- and bidentate ligands **L3** and **L5** turned out to perform best in the model reaction. There were two reasons for our decision to use this type of ligands, especially with adamantyl substituents: Firstly, adamantyl-substituted phosphine groups are in general quite air-stable and can be handled conveniently and even be exposed to air for some time. Secondly, such bulky nucleophilic phosphines bind more stably to the palladium center compared to triarylphosphines, thereby preventing agglomeration to palladium particles.



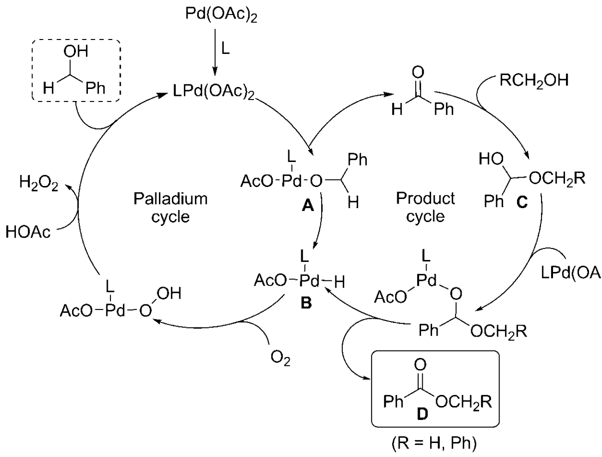
Scheme 3. Ligands (**L**) tested in Pd-catalyzed oxidative esterfications.

To our delight, a highly chemoselective oxidation (88% yield of methyl benzoate, **2a**) took place in the presence of *n*BuP(1-adamantyl)$_2$ (**L3**, cata*CX*iumA)[14] and $AgPF_6$ (Table 1, entry 11). On the other hand, application of the same ligand without $AgPF_6$ using toluene as solvent gave exclusively benzaldehyde in 84% yield (>99% selectivity). In this respect, it is interesting to note that Pd^0 complexes of cata*CX*iumA easily form the corresponding palladium–peroxo complex in the presence of dioxygen at room temperature.[15] However, this defined complex does not form any oxidation products upon reaction with benzyl alcohol (Scheme 4).



Scheme 4. Stoichiometric oxidative esterfication of benzylic alcohol by Pd^{II}.

Notably, using 1,1′-bis(di-*tert*-butylphosphino)-*o*-xylene (**L5**) as ligand and $AgPF_6$, oxidative esterification proceeded smoothly in toluene to give benzyl benzoate (**3a**) in 85% yield (Table 1, entry 16). Hence, by switching from **L3** to **L5**, highly selective oxidations towards the aldehyde and the different esters are achieved (Scheme 3). In Scheme 5 the proposed mechanism for these different reaction pathways is shown: the ligated Pd^{II} complex of benzyl alcohol **A** will undergo β-hydride elimination to form benzaldehyde and **B**. Reoxidation of complex **B** forms the active Pd catalyst again.

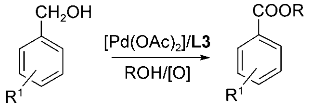


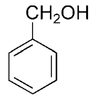
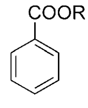
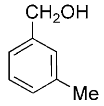
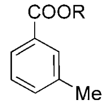
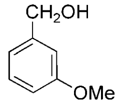
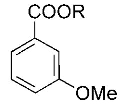
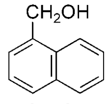
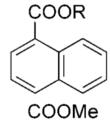
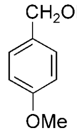
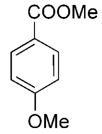
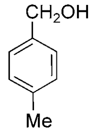
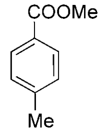
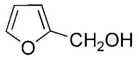
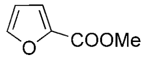
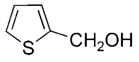
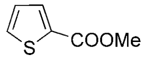
Scheme 5. Proposed mechanism of the oxidative esterification.

Depending on the reaction conditions, benzaldehyde can be oxidized further via hemiacetal **C**, which subsequently undergoes a second palladium-catalyzed oxidation to give ester **D** and **B**. Finally, **B** is reoxidized by dioxygen. It should be noted that after the reaction also the oxidized ligand is detected by ^{31}P NMR spectroscopy.[16]

To demonstrate the general applicability of the [Pd(OAc)$_2$]/cataCXium A system, various benzylic alcohols were tested in cross-esterification reactions with methanol and other aliphatic alcohols. In general, catalytic experiments were done in the presence of 2 mol% of Pd and 4 mol% of ligand at 50–60 °C under dioxygen atmosphere. As shown in Table 2, benzyl alcohol reacts smoothly with methanol, [D$_4$]methanol, ethanol, and 1,1,1-trifluoroethanol; these reactions give the desired products in high yields (Table 2, entries 1–4; 71–86 %). Notably, also less reactive, higher alcohols such as *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol give the desired products in moderate to good yields (52–88 %). Similarly, substituted benzyl alcohols and heterobenzyl alcohols gave the corresponding methyl esters in good yield (Table 2, entries 9–18).

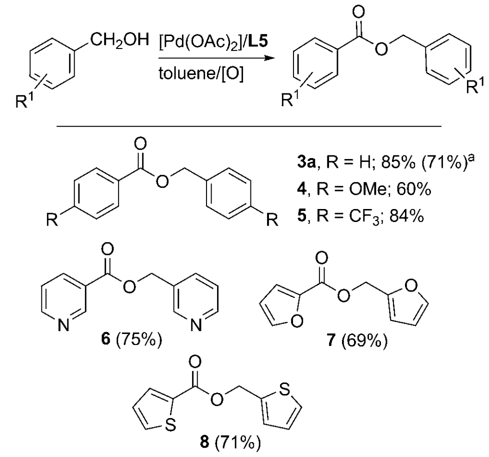
Table 2: Oxidative cross-esterification of benzyl alcohols.[a]



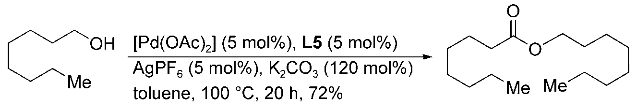
Entry	Substrate	Product		Cond.[a]	Yield [%][b,d]
1			R = Me	a	86(80)[c]
2			R = CD$_3$	a	83
3			R = Et	a	81
4			R = CH$_2$CF$_3$	a	71
5			R = *n*-propyl	b	53
6			R = *n*Bu	c	52
7			R = *n*-pentyl	b	88
8			R = *n*-hexyl	b	82
9			R = *n*Bu	b	85
10			R = *n*-hexyl	b	69
11			R = *n*Bu	b	82
12			R = *n*-pentyl	b	60
13			R = Me	b	75
14			R = *n*-propyl	b	54
15				a	63
16				a	84
17				a	61
18				b	72

[a] Reaction conditions a: 2 mol% Pd(OAc)$_2$, 4 mol% **L3**, 4 mol% AgPF$_6$, 50 mol% K$_2$CO$_3$, 3 mL ROH, 50–60 °C, 1 bar O$_2$. Conditions b: 5 mol% [Pd(OAc)$_2$], 5 mol% **L3**, 10 mol% AgPF$_6$, 100 mol% K$_2$CO$_3$, 3 mL ROH, 80 °C, 1 bar O$_2$. Conditions c: 5 mol% Pd(OAc)$_2$, 5 mol% **L3**, 10 mol% AgPF$_6$, 120 mol% K$_2$CO$_3$, 1 mL *n*BuOH, 80 °C, 4 bar O$_2$. [b] Yield of isolated product. [c] Reaction carried out on a 1 gram scale. [d] 20–40 h, complete consumption of starting material as monitored by TLC and GC–MS analysis.

Next, the oxidative homocoupling of different benzyl and heterobenzyl alcohols was performed with the optimized catalyst system that comprises [Pd(OAc)$_2$] and 1,1′-bis(di-*tert*-butylphosphino)-*o*-xylene (**L5**, Scheme 6). Indeed, the corresponding benzoate esters are formed in 60–85 % yield. There is no real trend of the catalyst performance depending on the electronic structure of the substrates. Finally, we demonstrated that oxidative homocoupling reactions are also possible with aliphatic alcohols as shown in Scheme 7. In preliminary experiments with 1-octanol, the desired ester is formed in 72 % yield at slightly higher temperatures (100 °C).



Scheme 6. Oxidative "self"-esterification of benzylic alcohols (reaction conditions: 5 mol% Pd(OAc)$_2$, 5 mol% **L5**, 5 mol% AgPF$_6$, 120 mol% K$_2$CO$_3$, toluene, 110 °C, 1 bar O$_2$). Yields refer to isolated products. [a] Reaction carried out on a 1 gram scale.



Scheme 7. Oxidative homocoupling of 1-octanol to octyl octanoate.

In conclusion, we have developed new palladium-catalyzed oxidative esterification reactions of primary alcohols with dioxygen as benign oxidant. Depending on the catalyst system, highly selective formation of the corresponding aldehydes or esters is observed. Both oxidative homocoupling reactions as well as cross-esterifications of benzyl alcohols with various aliphatic alcohols proceed under mild conditions (50–100 °C, 1 bar oxygen) to give the corresponding esters with water as the only side-product.

Notably, these novel atom-efficient and selective oxidation methods take place in the presence of commercially available ligands without the need of additional organic hydrogen acceptors.

Experimental Section

General procedure for oxidative “cross”-esterifications: An oven-dried 10 mL vial tube was charged with [Pd(OAc)$_2$] (12 mg, 0.050 mmol, 2 mol%), ligand **L3** (39 mg, 0.108 mmol, 4 mol%), AgPF$_6$ (27 mg, 0.108 mmol, 4 mol%), and K$_2$CO$_3$ (186 mg, 1.35 mmol, 0.5 equiv). The vial tube was sealed with a septum, evacuated and refilled with oxygen. Methanol (3 mL) and benzyl alcohol (300 mg, 2.70 mmol, 1.0 equiv), were added by a syringe. The reaction mixture was stirred at 50–60 °C for 20 h in the presence of an oxygen balloon. After cooling to room temperature, the reaction mixture was diluted with water and extracted with 50 mL of ethyl acetate. The combined organic layers were subsequently concentrated and the crude product was purified by flash chromatography.

General procedure for oxidative “self” esterification of benzylic alcohols: In an oven-dried 10 mL round-bottom flask, [Pd(OAc)$_2$] (31 mg, 0.139 mmol, 5 mol%), ligand **L5** (55 mg, 0.139 mmol, 5 mol%), AgPF$_6$ (33 mg, 0.139 mmol, 5 mol%), K$_2$CO$_3$ (458 mg, 3.32 mmol, 1.2 equiv), and benzyl alcohol (300 mg, 2.77 mmol, 1.0 equiv) were dissolved in 6 mL of toluene. The round-bottom flask was fitted with a condenser. The reaction mixture was stirred at 100 °C for 20 h in the presence of an oxygen balloon. After cooling to room temperature, the reaction mixture was diluted with water and extracted with 50 mL of ethyl acetate. The combined organic layers were subsequently concentrated and the crude product was purified by flash chromatography.

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Keywords: alcohols · aldehydes · esters · oxidative esterification · palladium

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