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EDGE ARTICLE

# General palladium-catalyzed aerobic dehydrogenation to generate double bonds†

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We describe a general dehydrogenation procedure to form  $\alpha,\beta$ -unsaturated aldehydes, ketones, esters and azobenzenes under very mild conditions, requiring catalytic commercial Pd(OAc)<sub>2</sub>, a catalytic weak inorganic base and air as the sole oxidant. In the presence of a diazafluorenone ligand, this process converts aliphatic aldehydes to  $\alpha,\beta$ -unsaturated aldehydes in an open-flask fashion at ambient pressure and temperature. A broad spectrum of substrates, including aldehydes, ketones, esters, alcohols and hydrazines, were conveniently dehydrogenated under a relatively uniformed protocol. A mechanism involving  $\beta$ -elimination-driven enolization equilibrium shift was proposed.

## Introduction

Olefins and carbonyls are perhaps two most versatile functional groups for organic transformations. Combined in conjugation,  $\alpha,\beta$ -unsaturated carbonyl compounds are capable of participating in a vast collection of organic reactions, particularly those creating carbon–carbon and carbon–hetero atom bonds.<sup>1</sup> Despite numerous methodologies for the preparation of various  $\alpha,\beta$ -unsaturated carbonyl compounds in the literature, such as the Peterson olefination,<sup>2</sup> the formylation,<sup>3,4</sup> or the cross-metathesis reactions of acrolein,<sup>5</sup> highly efficient preparation under mild and green conditions is still lacking.

Since Crabtree and Felkin discovered the first catalytic homogeneous dehydrogenation of cyclooctane to cyclooctene in the early eighties, tremendous progress has been made in the field of catalytic dehydrogenation of alkanes to olefins through transition metal catalysis.<sup>6,7</sup> In particular, Goldman and Brookhart advanced the scope and efficiency of catalytic alkane dehydrogenation using novel iridium pincer complexes.<sup>8</sup> These reactions are usually air-sensitive and require high temperature or pressure. Recent developments in the field of palladium(II) catalysis have emerged as an attractive alternative for the dehydrogenation of saturated carbonyl substrates, which is considered more practical.<sup>9</sup> Stoichiometric amounts of terminal oxidants (metal-based oxidants, peroxides, *etc.*) were initially employed to turnover palladium(II), followed by the more recent development of aerobic oxidation, where air or oxygen was

conveniently utilized as the oxidant. However, most reactions in the literature require rather harsh conditions when heating and a strong base is generally required. More puzzlingly, various recipes were summoned to accommodate a diverse substrate pool. Therefore, a straightforward protocol accommodating various functional groups for this important type of reaction is highly desirable. Recently, inspiring reports by Stahl and co-workers described relatively simple systems utilizing Pd(TFA)<sub>2</sub> (TFA = trifluoroacetate) for the selective synthesis of phenols and cyclic enones from saturated cyclic ketones. Their work represents a significant advance in terms of practicality and chemoselectivity. Nevertheless, a relatively high temperature was required and an unusual 2-amino-substituted pyridine ligand, or DMSO in case of cyclic enone synthesis, was employed to ensure good conversions and substrates were limited to only cyclic ketones.<sup>10</sup> We envision that through a similar reaction mechanism, a practical and green dehydrogenation reaction covering various activating groups would be highly likely and, herein, we report our initial results on substrates bearing aldehyde, ketone, alcohol, ester and hydrazine functionalities.

## Results and discussion

A general, mild and direct catalytic route to introduce both olefin and carbonyl groups in a cascade dehydrogenation would be highly desirable. We envisioned that air could be used as the sole oxidant and an ambient procedure would be ideal for an open-flask, green oxidation reaction.<sup>11,12</sup> With this goal as our initial target, we set out to screen metal catalysts using phenyl propionaldehyde as the substrate. From the preliminary results, palladium stood out as the most efficient metal for this transformation (Table 1).<sup>13</sup>

After we had identified Pd as the best metal for this process, we examined other reaction parameters (Table 2). Quick solvent screening revealed that only solvents DMF or DMSO led to

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**Table 1** Reaction condition optimization: catalyst

Entry	Metal	Conv. (%) <sup>a</sup>
1	CuBr	<5
2	Cu(OTf) <sub>2</sub>	<5
3	Ni(OAc) <sub>2</sub>	<5
4	Fe(OAc) <sub>3</sub>	<5
5	Sc(OTf) <sub>3</sub>	<5
6	[Rh <sub>2</sub> (COD)Cl] <sub>2</sub> <sup>b</sup>	<5
7	Ir(COD) <sub>2</sub> (μ-Cl) <sub>2</sub>	10
8	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub>	5
9	Pd(OAc) <sub>2</sub>	50

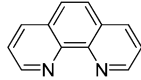

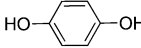
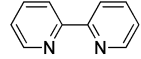
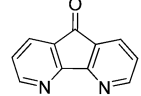
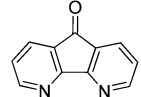
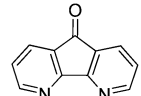
<sup>a</sup> Conversions were calculated by GC using biphenyl as the external standard. <sup>b</sup> Ligand, COD = 1,5-cyclooctadiene.

a noticeable conversion. Most weak bases were capable of catalyzing this reaction, with K<sub>2</sub>CO<sub>3</sub> being the most practical. Ligands seemed to help stabilize palladium species. Both phenols and diazafluorenone ligands were excellent ligands. In particular, the use of the 4,5-diazafluorenone ligand<sup>14</sup> led to an excellent yield at 30 °C (Table 2, entry 27). Interestingly, this ligand only worked well at a low temperature. Once heated to over 60 °C, the reaction conversion drastically decreased (Table 2, entries 26 and 28). In most cases, aldol dimerization/oligomerization was the major competing side reaction and the oxidation of aldehydes to acids was negligible.

This mild aerobic dehydrogenation was general for various β-aryl aldehydes (Table 3). The reactions proceeded faster at elevated temperature (*i.e.* 60 °C). However, the aldol dimerization side reaction started to intervene and the starting aldehyde and α,β-unsaturated aldehyde products also slowly decomposed over time. Lowering the reaction temperature to near room temperature conveniently overcame those hurdles. The reactions of aldehydes were carried out in an open-flask manner at 30 °C. A small amount of water did not affect the reaction time and isolated yields. Reagent-grade DMF could be used without purification. We observed a small degree of rate decrease when the aromatic rings were either electron rich or *o*-substituted. The employment of the 4,5-diazafluorenone ligand was critical to maintaining high yields, as well as suppressing the decomposition of relatively unstable cinnamaldehyde products.

Next, we challenged this rather simple catalytic system with more inert substrates. Ketones were more difficult substrates in previous reports,<sup>10b,13,15</sup> possibly due to the weaker acidity of the α-carbon C–H relative to aldehydes. Most recently, cyclic ketones have been demonstrated to undergo smooth dehydrogenation using DMSO as a ligand. We were delighted to find that simply using 6 mol% palladium acetate and 10 mol% potassium carbonate we were able to obtain α,β-unsaturated ketones in high yields at 110 °C (Table 4). The reactions were very slow at room temperature. As mentioned earlier, the 4,5-diazafluorenone ligand stopped facilitating this reaction at 60 °C and above and conversions using this ligand were poor under those conditions. We reason that oxidation of the ligand to the *N*-oxide

**Table 2** Reaction condition optimization: ligand and base

Entry <sup>a</sup>	Catalyst	Base	Ligand	Conv. (%) <sup>b</sup>
1	PdCl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	—	6
2	PdBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	—	30
3	PdI <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	—	16
4	Pd(dba) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	—	36
5	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	—	50
6	Pd(TFA) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	—	15
7	Pd(OAc) <sub>2</sub>	KHCO <sub>3</sub>	—	49
8	Pd(OAc) <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	—	29
9	Pd(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	—	47
10	Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub>	—	25
11	Pd(OAc) <sub>2</sub>	Na <sub>3</sub> PO <sub>4</sub>	—	30
12	Pd(OAc) <sub>2</sub>	Na <sub>2</sub> HPO <sub>4</sub>	—	22
13	Pd(OAc) <sub>2</sub>	NaH <sub>2</sub> PO <sub>4</sub>	—	11
14	Pd(OAc) <sub>2</sub>	KF	—	38
15	Pd(OAc) <sub>2</sub>	TBAF	—	24
16	Pd(OAc) <sub>2</sub>	MgO	—	26
17	Pd(PPh <sub>3</sub> )Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	—	59
18	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub>	65
19	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>		18
20	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	57
21	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	BINOL	44
22	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	Me–NH–HN–Me	35
23	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>		72
24	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>		69
25	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>		45
26	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>		79
27	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>		90 <sup>c</sup>
28	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>		<5 <sup>d,e</sup>

<sup>a</sup> All reactions were carried out at 60 °C for 8 h in a 2 dram vial open to air. <sup>b</sup> Conversions were calculated by GC using biphenyl as the external standard. <sup>c</sup> Reaction was carried out at 30 °C for 24 h. <sup>d</sup> Reaction was carried out at 110 °C for 12 h. <sup>e</sup> Substrates decomposed rapidly, presumably through the competing aldol reaction.

at high temperature might partially poison the palladium catalysts. Nevertheless, the ligand-free conditions were able to render the desired α,β-unsaturated ketones in good to excellent yields.

**Table 3** Aerobic dehydrogenation of aldehydes

Entry	Ar	Time (h) <sup>a</sup>	Yield (%) <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> , <b>1a</b>	36	86
2	4-EtOOC-C <sub>6</sub> H <sub>4</sub> , <b>1b</b>	24	84
3	4-MeOC-C <sub>6</sub> H <sub>4</sub> , <b>1c</b>	24	87
4	4-MeO-C <sub>6</sub> H <sub>4</sub> , <b>1d</b>	24	77
5	3-Me-C <sub>6</sub> H <sub>4</sub> , <b>1e</b>	36	88
6	2,4-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> , <b>1f</b>	36	78
7	2,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> , <b>1g</b>	36	66

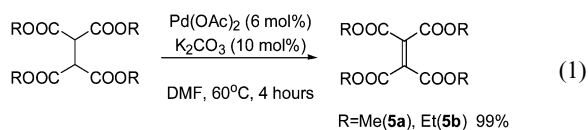
<sup>a</sup> All reactions were carried out in a 2 dram vial open to air. <sup>b</sup> Isolated yields after flash column chromatography.

**Table 4** Aerobic dehydrogenation of ketones

Entry	Ar	Time (h)	Yield (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> , <b>3a</b>	24	92
2	4-Br-C <sub>6</sub> H <sub>4</sub> , <b>3b</b>	24	81
3	4-Cl-C <sub>6</sub> H <sub>4</sub> , <b>3c</b>	48	82
4	4-MeO-C <sub>6</sub> H <sub>4</sub> , <b>3d</b>	48	67
5	2-Me-C <sub>6</sub> H <sub>4</sub> , <b>3e</b>	48	71
6	2,4-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> , <b>3f</b>	48	62
7	2,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> , <b>3g</b>	48	86 <sup>b</sup>
8	2-F-C <sub>6</sub> H <sub>4</sub> , <b>3h</b>	48	72 <sup>b</sup>
9	2-C <sub>10</sub> H <sub>7</sub> , <b>3i</b>	48	53 <sup>b</sup>
10	2-C <sub>5</sub> H <sub>4</sub> N, <b>3j</b>	24	81 <sup>b</sup>
11	2-C <sub>9</sub> H <sub>6</sub> N, <b>3k</b>	24	95 <sup>b</sup>

<sup>a</sup> All reactions were carried out in a 2 dram vial open to air. <sup>b</sup> Reactions were done under an oxygen balloon.

More excitingly, even esters were successfully dehydrogenated as well. To the best of our knowledge, there is no report on the direct catalytic aerobic dehydrogenation of esters. Quantitative yields were observed for tetra-esters in open-flask reactions at 60 °C after 4 h. Dehydrogenation of tri-esters and di-esters were also successful (eqn (1)) and the products underwent *in situ* Michael addition to form the cascade products (see supporting information for additional information, example 5c and 5d<sup>†</sup>). Mono-esters failed to undergo dehydrogenation under the described conditions.



Besides carbon–carbon bond dehydrogenation, this general protocol can also be applied to abstract hydrogen off carbon–hetero atom bonds and hetero–hetero atom bonds (Scheme 1):

(1) Diphenyl methanol was converted to the corresponding diphenyl ketone in a quantitative yield.<sup>16,17</sup>

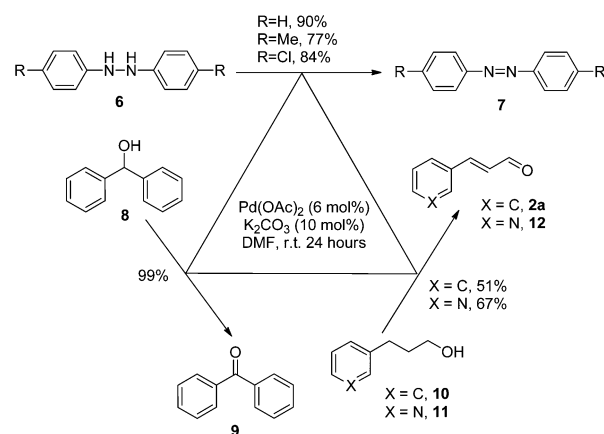
(2) Phenyl propanol was able to undergo double dehydrogenation to render cinnamaldehyde in a single step.<sup>13c</sup> Heterocyclic substitutions are also tolerated (substrate **11**).

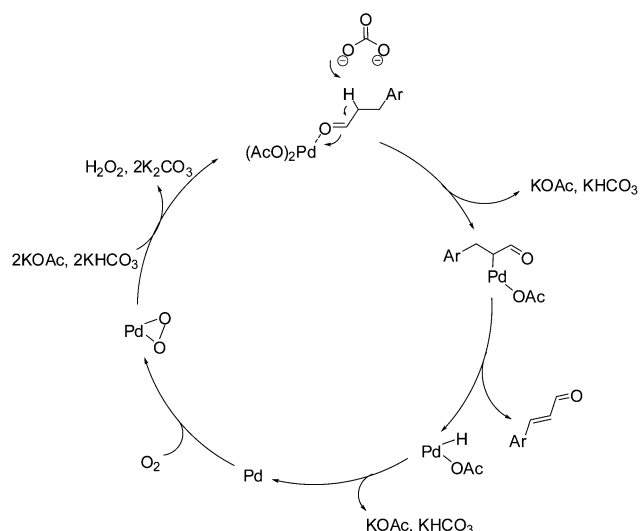
(3) Hydrazines were also excellent substrates. Although Jiao *et al.* reported that palladium would not catalyze the conversion from aniline to azobenzene,<sup>18</sup> the second step of their copper-catalyzed reaction was readily catalyzed under our Pd(OAc)<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub> protocol. Various hydrazines reacted at room temperature and generated azobenzenes in good to high yields.

Presumably, this palladium(II)-catalyzed process could operate through the Saegusa mechanistic cycle: generation of palladium enolate followed by β-hydride elimination.<sup>19,10b</sup> We believe this catalytic cycle was made possible through a Lewis acid promoted activation of β-α-proton<sup>20,21</sup> (Scheme 2). In our case, Pd(OAc)<sub>2</sub> was sufficient to lower the pK<sub>a</sub>'s of the α-carbon of aldehydes/ketones to the level that it would form an appreciable equilibrium with their enolate forms in the presence of K<sub>2</sub>CO<sub>3</sub>. It is unclear how O<sub>2</sub> interacts with the Pd center; HOOPd(OAc) may act as active species rather than to Pd(OAc)<sub>2</sub>.<sup>22</sup> The α,β-unsaturated carbonyls could also act as ligands to stabilize palladium.

Several other oxidants were examined; both air and oxygen proved to be the best terminal oxidant. The catalytic potassium carbonate is critical since a stoichiometric amount of base resulted in significant aldol side reactions for aldehyde substrates. NMR monitoring experiments indicated that aldehydes decomposed rapidly in the presence of K<sub>2</sub>CO<sub>3</sub> in DMF under air. However, the addition of Pd(OAc)<sub>2</sub> resulted in clean dehydrogenation (see supporting information for additional information, Figs S1 and S2<sup>†</sup>). Other Lewis acids were briefly examined, most of them failed due to an intolerance to K<sub>2</sub>CO<sub>3</sub>, suggesting that the subtle balance between Lewis acidity and basicity was one of the determining factors to a successful catalytic cycle.

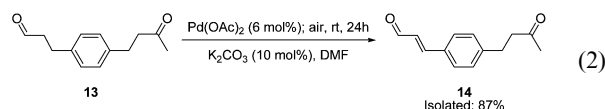
To demonstrate the selective nature of this dehydrogenation reaction, substrate **13** was synthesized and subjected to our reaction condition. Only the α,β-unsaturated aldehyde was

**Scheme 1** Dehydrogenation to heteroatom-containing double bonds.



**Scheme 2** The proposed mechanism of palladium(II)/base pair-catalyzed dehydrogenation of aldehydes.

observed and isolated in good yield after 24 h at room temperature (eqn (2)).



## Conclusions

In summary, we established a general, simple, yet practical protocol that allows convenient aerobic dehydrogenation of aldehydes, ketones, esters, alcohols and hydrazines. The reactions employed a catalytic amount of both palladium acetate and cheap inorganic base. The reactions were carried out at ambient pressure in mild open-flask practice. The direct catalytic generation of  $\alpha,\beta$ -unsaturated monoesters is under way. Further studies on the reaction mechanisms and applications in cascade reactions are currently ongoing and will be reported in due course.

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