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3,4-Alkadienyl Ketones via the Palladium-Catalyzed Decarboxylative Allenylation of 3-Oxocarboxylic acids

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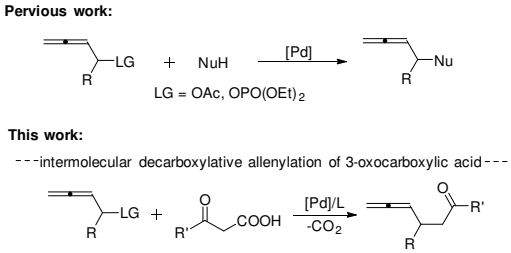
In this communication, we will report a palladium-catalyzed decarboxylative allenylation of benzyl carbonates and *tert*-butyl carbonates of 2,3-allenol with 3-oxocarboxylic acid. The reaction provides a new and straightforward approach to 3,4-dienyl ketones under mild conditions.

Allenes are particularly attractive building blocks in organic synthesis because of their ability to undergo a variety of transformations.[1] Thus, the development of efficient methods for the synthesis of functional allenes is of high interest. So far, the methods for the synthesis of allenones, especially 3,4-dienyl ketones, have not been well established. In general, they are synthesized stepwise by α-allenylation of 1,3-dicarbonyl compounds or imines with buta-2,3-dienyl bromide followed by corresponding decarbonylation or hydrolysis;[2] S_N2'-type substitution of α-imido lithium organocuprates with diethyl buta-1,3-dien-2-yl phosphonate or 3-(1,3-dioxolan-2-yl)-alkyl magnesium bromide with propargylic bromides followed by hydrolysis;[3] S_N2 substitution of allenyllithium with 4-(1,3-dioxolan-2-yl)-alkyl bromide and hydrolysis;[4] dibromomethylation of the acetals of ω-alken-2-ones treated with methyllithium or magnesium;[5] sequential 1,2-addition of carbon nucleophiles to β-carbonyl cyclohexenol triflates, C-C fragmentation and β- elimination.[6] In addition, oxidation of the alka-4,5-dienols may produce the corresponding 3,4-allenyl ketones.[4,7] All these methods suffer from multi-steps and not-really-available starting materials. Thus, there is an urgent demand for the development of a convenient and efficient synthesis of 3,4-allenones under mild conditions from really available starting materials.

Recently, much attention has been paid to the transition metal-catalyzed reaction of 2,3-allenyl compounds with leaving groups and nucleophiles, such as 1,3-dicarbonyl compounds[8] or amines,[8b,9] affording allenes with a nucleophilic functionality. Inspired by these previous works and our interest on allene synthesis, we herein report a palladium-catalyzed intermolecular decarboxylative allenylation of 3-oxocarboxylic acids[10] for the efficient synthesis of 3,4-allenones under mild reaction conditions.



Scheme 1. Palladium-catalyzed nucleophilic allenylation and intermolecular decarboxylative allenylation to synthesize 3,4-allenones.

Our investigation began with the reaction of nona-1,2-dien-4-yl acetate **1a** and 3-phenyl-3-oxopropanoic acid **2a**. Initially, we optimized the reaction condition by screening different ligands combined with $Pd_2(dba)_3{\cdot}CHCl_3$ as catalyst and $LiOBu^t$ as base in THF at 25 °C (Table 1, Entries 1-8). We found that **L8** was the best ligand of this reaction, which afforded the decarboxylated product **3aa** in 55% NMR yield (Table 1, Entry 8). The normal expected product **3aa'** was not detected in the crude reaction mixture. Although the yield of **3aa** with ligand **L7** (54%, Table 1, Entry 7) was slightly lower than **L8**, it was far cheaper,[11] so we chose **L7** as the ligand for further optimization. Further screening of other palladium sources (Table 1, Entries 9-12), such as [Pd(π-cinnamyl)Cl]$_2$, [Pd(allyl)Cl]$_2$, $Pd(OAc)_2$ and $Pd(PPh_3)_4$, showed that $Pd_2(dba)_3{\cdot}CHCl_3$ is still the best.

Using 2.5 mol% $Pd_2(dba)_3{\cdot}CHCl_3$ and 10 mol% binap (**L7**) as the catalyst and 2.0 equiv. of $LiOBu^t$ as the base, subsequent

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† Footnotes relating to the title and/or authors should appear here.
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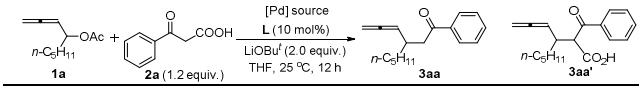
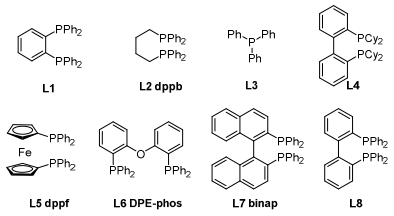
Table 1. Effect of catalyst and ligand.[a]



Entry	[Pd] (mol%)	L	Yield of **3aa**(%)[b]	Recovery of **1a** (%)[b]
1	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	**L1**	0	69
2	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	**L2**	2	43
3	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	**L3**	4	72
4	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	**L4**	9	38
5	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	**L5**	23	0
6	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	**L6**	42	0
7	**$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)**	**L7**	**54**	**0**
8	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	**L8**	55	0
9	$[Pd(\pi\text{-cinnamyl})Cl]_2$(2.5)	**L7**	7	68
10	$[Pd(allyl)Cl]_2$(2.5)	**L7**	7	57
11	$Pd(OAc)_2$ (5)	**L7**	15	55
12	$Pd(PPh_3)_4$ (5)	**L7**	49	0

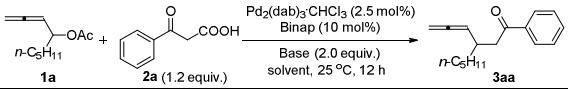
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.2 equiv.), Pd catalyst (2.5 or 5 mol%), ligand (10 mol%), and LiOBu^t (2.0 equiv.) in THF (1 mL) at 25 °C for 12 h. [b]Determined by NMR analysis of the crude using mesitylene as the internal standard.



study on the solvent effect indicated that the reaction in THF afforded **3aa** in 54% NMR yield (Table 2, Entry 13). When Li_2CO_3 and $LiOH{\cdot}H_2O$ were used, recovery of nona-1,2-dien-4-yl acetate **1a** in corresponding 48% and 62% NMR yield was observed (Table 2, Entries 9 and 10). However, when NaOBu^t or KOBu^t were used, the reactions were complicated (Table 2, Entries 11 and 12), and no expected product **3aa** was detected.

Further study was directed to the effect of leaving group, various esters of nona-1,2-dien-4-ol **1a-e** were used (Table 3, Entries 1-4, 11). When the leaving group was OCbz, **3aa** could be afforded in 75% NMR yield (Table 3, Entry 11). When the reaction was reacted without $Pd_2(dba)_3{\cdot}CHCl_3$ and binap, **3aa** was not detected and the **1e** was almost completely recycled (Table 3, Entry 5). Inspired by above results, we further optimized the loading of catalyst, ligand and base (Table 3, Entries 6-12), and found that the optimal reaction conditions involved 2.5 mol% $Pd_2(dba)_3{\cdot}CHCl_3$, 7.5 mol% binap (**L7**), and2.0 equiv. LiOBut in THF at 25 °C with OCbz as the best leaving group (Table 3, Entry 12). When we replaced $Pd_2(dba)_3{\cdot}CHCl_3$ with $Cu(OAc)_2{\cdot}H_2O$ or $Ni(OAc)_2{\cdot}4H_2O$, the 3,4-alkadienyl ketone **3aa** was not be observed and the **1e** was almost completely recycled(Table 4, Entries 12 and 13). However, the the amount of **2a** was increased to 1.5 equivalent of **1e**, the NMR yield of decarboxylated product **3aa** was decreased to 68%(Table 4, Entry 14).

Table 2. Effect of base and solvent.[a]



Entry	Base	Solvent	Yield of **3aa** (%)[b]	Recovery of **1a** (%)[b]
1	LiOBu^t	MeCN	0	34
2	LiOBu^t	DCM[c]	0	42
3	LiOBu^t	DMSO[d]	17	0
4	LiOBu^t	Et_2O	21	<14
5	LiOBu^t	MTBE[e]	24	5
6	LiOBu^t	Toluene	26	<15
7	LiOBu^t	1,4-Dioxane	27	31
8	LiOBu^t	DME[f]	48	0
9	Li_2CO_3	THF[g]	0	48
10	$LiOH{\cdot}H_2O$	THF	5	62
11	NaOBu^t	THF	complicated	
12	KOBu^t	THF	complicated	
13	LiOBu^t	**THF**	**54**	**0**

[a] Reaction conditions : **1a** (0.2 mmol), **2a** (1.2 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$(2.5 mol%), binap (10 mol%), and base (2.0 equiv.) in solvent (1 mL) at 25 °C for 12 h. [b]Determined by NMR analysis of the crude using mesitylene as the internal standard. [c]DCM = Dichloromethane. [d]DMSO = Dimethyl sulfoxide. [e]MTBE = *Tert*-butyl methyl ether. [f]DME = 1,2-Dimethoxyethane. [g] THF = Tetrahydrofuran.

With the optimized conditions in hand, the scope of this reaction has been investigated and the results are summarized in Table 4. When R^1 group is *n*-C_5H_{11} or *n*-C_6H_{13} and Ar is phenyl, the reaction afforded the corresponding products **3aa** and **3fa** in 79% yields (Table 4, Entries 1 and 2); moreover, alkyl group R^1 with many synthetically useful functional groups, such as OTHP, OBn, C=C bond and C-C triple bond may be accommodated (Table 4, Entries 6-9); R^1 may be also aryl groups bearing halide, COOMe, CN (**1m-r**) generating the corresponding products in 44-62% yields (Table 4, Entries 10-15). For the scope of Ar, synthetically attractive Br (**2b**) or Cl (**2c**) could be accommodated (Table 4, Entries 4 and 5), however, it is worth noting that the reaction should be conducted at 50 °C; Ar may also be 2-thienyl group (**2g**), 2-furyl group (**2h**), or 2-naphthyl (**2i**). Furthermore, we could easily conduct the reaction of 2.2 g (7.5 mmol) of **1f** to provide 1.26 g of **3fa** (Table 4, Entry 3). The reaction of *tert*-butyl dodeca-1,2-dien-5-yn-4-yl carbonate **1s** with 3-(naphthalen-2-yl)-3-oxopropanoic acid **2i** afforded the desired product **3si** in 49% yield (Table 4, Entry 16).

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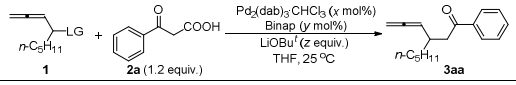
Table 3. Effect of leaving group and the loading of catalyst, ligand, and base.[a]



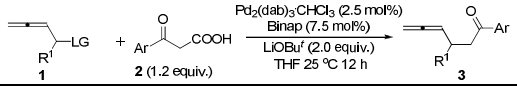
Entry	LG	[Pd]/L/Base (*x*/*y*/*z*)	Yield of **3aa** (%)[b]	Recovery of **1** (%)[b]
1	OAc **(1a)**	2.5/10/2	54	0
2	OCO_2Me **(1b)**	2.5/10/2	65	8
3	OBz **(1c)**	2.5/10/2	70	7
4	OBoc **(1d)**	2.5/10/2	72	0
5	OCbz **(1e)**	0/0/2	0	99
6	OCbz **(1e)**	2.5/7.5/1.2	21	32
7	OCbz **(1e)**	2/8/2	60	15
8	OCbz **(1e)**	3/12/2	61	0
9	OCbz **(1e)**	2.5/7.5/3	63	0
10	OCbz **(1e)**	2.5/5/2	70	0
11	OCbz **(1e)**	2.5/10/2	75	0
12[c]	OCbz **(1e)**	5/7.5/2	0	91
13[d]	OCbz **(1e)**	5/7.5/2	0	94
14[e]	OCbz **(1e)**	2.5/7.5/2	68	0
15	**OCbz (1e)**	**2.5/7.5/2**	**80**	**0**

[a]LG = Leaving group, Reaction conditions: **1** (0.2 mmol), **2a** (1.2 equiv.), $Pd_2dba)_3{\cdot}CHCl_3$(*x* mol%), Binap (*y* mol%), and $LiOBu^t$ (*z* equiv.) in THF (1 mL) at 25 °C for 12 hours. [b]Determined by NMR analysis of the crude using mesitylene as the internal standard. [c]$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol%) was replaced with $Cu(OAc)_2{\cdot}H_2O$(5 mol%). [d]$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol%) was replaced with $Ni(OAc)_2{\cdot}4H_2O$(5 mol%). [e] 1.5 equivalent of **2a** were used.

To understand the mechanism of the reaction, we tried the reaction of benzyl deca-1,2-dien-4-yl carbonate **1f** with acetophenone **4a** under standard conditions. It was found that no desired product **3fa** was formed (Scheme 2, Eq. 1). When 3-oxocarboxylic acid **2a** was directly stirred in THF, acetophenone was generated in 5% NMR yield after 12 h (Scheme 2, Eq. 2a). However, in the presence of $Pd_2dba)_3{\cdot}CHCl_3$ and binap, acetophenone was generated in 83% NMR yield with no D-incorporation upon quenched with D_2O (Scheme 2, Eq. 2b). Finally, we found that the reaction of **2a** with $LiOBu^t$ alone afforded acetophenone-d_3 in 62% yield and 75% of D-incorportion upon quenching with D_2O (Scheme 2, Eq. 2b). The reaction of acid **2d** with $Pd_2(dba)_3{\cdot}CHCl_3$ and binap showed the similar results of **2a,** however, its reaction with $LiOBu^t$ is much slower (Scheme 2, Eq. 3a and 3b).

Based the above results, a plausible mechanism is proposed as shown in Scheme 3. A methyleneallylic palladium(II) complex **A**[12] was formed via the oxidative addition of **1** with the Pd(0) catalyst. Then, there are two possible pathways. **Path A**: The complex **A** undergoes the ligand exchange to form methyleneallylic palladium(II) 3-oxocarboxylate **B.** After the decarboxylation, methyleneallylic palladium(II) enolate intermediate **C** is formed (see Eq. 2b and 3a). **Path B**: decarboxylation of 3-oxocarboxylic acid **2** occurs under existence of base to form the enolate **2'** first (see Eq. 2c and 3b), which undergoes the subsequent ligand exchange with complex **A** to form intermediate **C**. Reductive elimination would give the final product **3** and regenerate the Pd(0) catalyst to complete the catalytic cycle.

Table 4. Synthesis of 3,4-allenyl ketones by decarboxylative allenylation of 3-oxoacarboxylic acids.[a]



Entry	**1**		**2**	Yield of **3** (%)[b]
	LG	R^1	Ar	
1	OCbz	*n*-C_5H_{11}**(1e)**	C_6H_5 **(2a)**	79**(3aa)**
2	OCbz	*n*-C_6H_{13}**(1f)**	C_6H_5 **(2a)**	79**(3fa)**
3[c]	OCbz	*n*-C_6H_{13}**(1f)**	C_6H_5 **(2a)**	65**(3fa)**
4[d]	OCbz	H**(1g)**	4-BrC_6H_4 **(2b)**	67**(3gb)**
5[d]	OCbz	$BnCH_2$**(1h)**	4-ClC_6H_4 **(2c)**	46**(3hc)**
6	OCbz	CH_2=$CH(CH_2)_8$**(1i)**	4-$CH_3OC_6H_4$ **(2d)**	53**(3id)**
7	OCbz	$THPO(CH_2)_5$**(1j)**	4-$CH_3C_6H_4$ **(2e)**	51**(3je)**
8	OCbz	$BnOCH_2$**(1k)**	3-$CH_3C_6H_4$ **(2f)**	56**(3kf)**
9	OCbz	TMSC≡$C(CH_2)_3$**(1l)**	C_6H_5 **(2a)**	62**(3la)**
10	OBoc[e]	C_6H_5**(1m)**	2-thienyl **(2g)**	48**(3mg)**
11	OBoc	4-FC_6H_4**(1n)**	2-furyl **(2h)**	44**(3nh)**
12	OBoc	3-BrC_6H_4**(1o)**	C_6H_5 **(2a)**	49**(3oa)**
13	OBoc	4-BrC_6H_4**(1p)**	C_6H_5 **(2a)**	59**(3pa)**
14	OBoc	4-$CH_3O_2CC_6H_4$**(1q)**	C_6H_5 **(2a)**	51**(3qa)**
15	OBoc	3-NCC_6H_4 **(1r)**	C_6H_5 **(2a)**	62**(3ra)**
16	OBoc	$CH_3(CH_2)_5C$≡C **(1s)**	2-naphthyl **(2i)**	49 **(3si)**

[a]Reaction conditions : **1**(1.0 mmol), **2** (1.2 equiv.), $Pd_2dba)_3{\cdot}CHCl_3$(2.5 mol%), Binap (7.5mol%), $LiOBu^t$ (2.0 equiv.) in THF (5 mL) at 25 °C for 12 h. [b]Isolated yield [c]Reaction conditions: **1f** (7.5 mmol), **2a** (1.2 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$(2.5 mol%), Binap (7.5 mol%), $LiOBu^t$ (2.0 equiv.) in THF (37.5 mL) at 25 °C for 12 h. [d]The reaction was at 50 °C. [e] The leaving group of **1m-s** is OBoc instead of OCbz owing to the fact that the corresponding benzyl carbonates of 2,3-allenol could not be prepared.

In conclusion, we have developed a palladium-catalyzed decarboxylative allenylation of benzyl carbonates or *tert*-butyl carbonates of 2,3-allenols with 3-oxocarboxylic acids. The reaction provides a new, straightforward approach to 3,4-dienyl ketones under mild conditions. Due to the esaily availablity of both starting materials and the catalyst as well as simple operation, this method will be useful in organic

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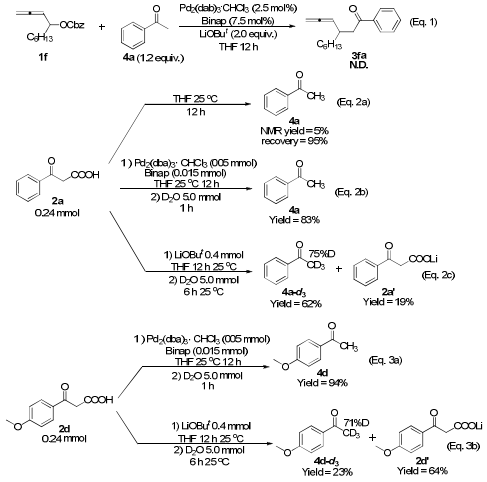
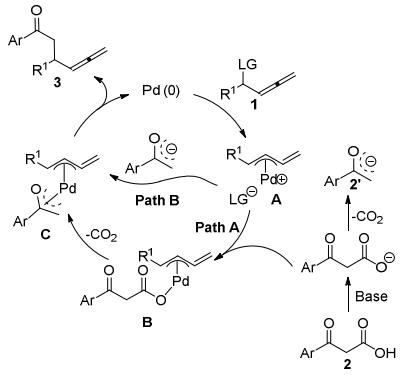
synthesis. Further studies to synthesize asymmetric 3,4-allenones via this protocol are ongoing in our laboratory.



Scheme 2. Control Experiment



Scheme 3. Proposed mechanism

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