



Palladium-catalyzed formal hydroacylation of allenes employing carboxylic anhydrides and hydrosilanes



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ABSTRACT

The formal hydroacylation reaction of allenes has been developed employing carboxylic anhydrides as acyl sources and hydrosilanes as reducing reagents in the presence of a commercially available palladium complex as a catalyst. The reaction affords α,β -unsaturated ketones regio- and stereoselectively. The similar catalyst system is also effective for the reduction of carboxylic anhydrides to the corresponding aldehydes employing hydrosilanes.

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1. Introduction

Hydroacylation reaction involving the addition of aldehydes to carbon–carbon multiple bonds is a useful synthetic method to provide unsymmetrical ketones atom-economically.¹ However, intermolecular hydroacylation of alkenes and alkynes often suffers from low selectivity and low yields. In order to ensure high efficiency, i) intramolecular reaction,² ii) substrates bearing suitable directing groups,³ and/or iii) carbon monoxide pressure,⁴ were often indispensable. An alternative method is a formal hydroacylation employing a suitable acyl source in place of an aldehyde. The oxidative or reductive formal hydroacylation employing alcohols as acyl donors were reported.⁵ We recently found the palladium-catalyzed formal hydroacylation of allenes employing acid chlorides and hydrosilanes.⁶ The reaction afforded the corresponding α,β -unsaturated ketones regio- and stereoselectively.

Carboxylic anhydrides are stable, easy-to-handled, and easy-to-prepare compounds from the corresponding carboxylic acids, and are one of the most useful compounds in organic synthesis. Regarding the transition-metal catalyzed reactions, it is known that the oxidative addition of the C(acyl)–O bond proceeds in the presence of suitable transition-metal complexes.⁷ Thus, carboxylic anhydrides were used as an acyl source in the palladium-catalyzed

cross-coupling reactions employing organoboronic acids⁸ and organozinc reagents.⁹ Carboxylic anhydrides were also utilized in the formal hydroacylation of styrene derivatives in the presence of a rhodium catalyst.¹⁰

Herein, we report the palladium-catalyzed formal hydroacylation of allenes employing carboxylic anhydrides with stable and easy-to-handle hydrosilanes as a reducing agent. As for the hydroacylation of allenes using aldehydes,¹¹ there have been only two precedents to date, in which the aldehydes must bear hydroxyl^{11a} or thioether^{11b} functionalities as directing groups. Noteworthy is that no directing groups are necessary in the present reaction.

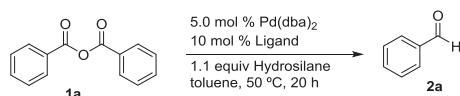
2. Palladium-catalyzed reduction of carboxylic anhydrides

Before investigating the formal hydroacylation of allenes, we carried out reduction of carboxylic anhydrides to aldehydes employing hydrosilanes as a reducing agent. Yamamoto and co-workers reported the reduction of carboxylic anhydrides to the corresponding aldehydes in the presence of palladium catalysts.¹² However, the reaction required high pressure (3.0 MPa) of molecular hydrogen. Based on our previous report that a palladium complex efficiently catalyzes the reduction of carboxylic acids in the presence of pivalic anhydride,¹³ Pd-catalyzed reduction of carboxylic anhydrides employing hydrosilanes to the corresponding aldehydes was carried out. Thus, benzoyl anhydride (**1a**) was treated with a mixture of Pd(dba)₂ and P(*p*-MeOC₆H₄)₃ as a catalyst in the presence of H₂SiMePh as a reducing agent in toluene at 50 °C

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(Table 1). As a result, benzaldehyde (**2a**) was obtained in 85% yield (entry 1). Without the ligand, **1a** did not convert at all (entry 2). As the ligand, PPh₃, P(*p*-MeOC₆H₄)₃ and PCy₃ also afforded **2a** in good yields (entries 3–5). As for hydrosilanes, HSiEt₃ afforded **2a** in 67% yield, while more bulky HSi^tPr₃ was not efficient (entries 6 and 7). H₂SiEt₂ and H₂SiPh₂ provided **2a** in 74% and 9% yields, respectively (entries 8 and 9). MeCN was also a good solvent in the reaction (entry 10).

Table 1
Effect of ligands and hydrosilanes on the palladium-catalyzed reduction of benzoic anhydride (**1a**)^a



Entry	Ligand	Hydrosilane	Yield (%) ^b
1	P(<i>p</i> -MeOC ₆ H ₄) ₃	H ₂ SiMePh	85
2	None	H ₂ SiMePh	Trace
3	PPh ₃	H ₂ SiMePh	68
4	P(<i>p</i> -MeOC ₆ H ₄) ₃	H ₂ SiMePh	74
5	PCy ₃	H ₂ SiMePh	66
6	P(<i>p</i> -MeOC ₆ H ₄) ₃	HSiEt ₃	67
7	P(<i>p</i> -MeOC ₆ H ₄) ₃	HSi ^t Pr ₃	14
8	P(<i>p</i> -MeOC ₆ H ₄) ₃	H ₂ SiEt ₂	74
9	P(<i>p</i> -MeOC ₆ H ₄) ₃	H ₂ SiPh ₂	9
10 ^c	P(<i>p</i> -MeOC ₆ H ₄) ₃	H ₂ SiMePh	81

^a Reaction conditions: benzoic anhydride (**1a**: 0.50 mmol), hydrosilane (0.55 mmol), Pd(dba)₂ (0.025 mmol, 5.0 mol %), ligand (0.05 mmol, 10 mol %, P/Pd=2) in toluene (1.0 mL) at 50 °C for 20 h.

^b Yield based on the GC internal standard technique.

^c MeCN (1.0 mL) was used as the solvent.

Various carboxylic anhydrides were smoothly converted to the corresponding aldehydes in good to high yields (Table 2). Among them, the reaction of an aromatic acid anhydride having an electron donating group (-OMe) proceeded smoothly, giving the corresponding aldehyde in 83% yield (entry 1). In the reaction of **1c** bearing an electron withdrawing group (-CF₃), **2c** was isolated in 52% yield (entry 2). 3-Pyridinecarboxylic anhydride **1d** gave **2d** in good yield (entry 3). With 3-arylpropionic acid anhydrides (**1e** and **1f**), the desired aldehydes (**2e** and **2f**) were obtained in good yields (entries 4–5). Other aliphatic acid anhydrides such as **1g**, **1h**, and **1i** also converted to the corresponding aldehydes in 88%, 93%, and 82% yields, respectively (entries 6–8). In addition, cyclohexane-carboxylic anhydride **1j** also afforded **2j** in 73% yield by elevating the

Table 2
The palladium-catalyzed reduction of carboxylic anhydrides to the corresponding aldehydes^a

Entry	Carboxylic anhydride (1)	Temp (°C)	Yield (%) ^b
1		50	2b :83
2 ^c		40	2c :52
3		40	2d :75
4		60	2e :76
5		40	2f :70

Table 2 (continued)

Entry	Carboxylic anhydride (1)	Temp (°C)	Yield (%) ^b
6		50	2g :88 ^d
7		50	2h :93 ^d
8		60	2i :82
9		120	2j :73 ^d

^a Reaction conditions: carboxylic anhydride (**1**: 0.50 mmol), H₂SiMePh (0.55 mmol), Pd(dba)₂ (0.025 mmol, 5.0 mol %), P(*p*-MeOC₆H₄)₃ (0.050 mmol, 10 mol %, P/Pd=2) in toluene (1.0 mL), for 20 h.

^b Isolated yield.

^c Pd(dba)₂ (0.05 mmol, 10 mol %), P(*p*-MeOC₆H₄)₃ (0.10 mmol, 20 mol %, P/Pd=2).

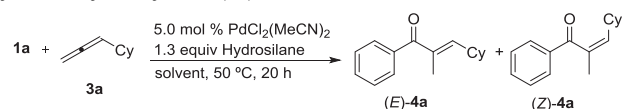
^d Yield based on the GC internal standard technique.

reaction temperature to 120 °C (entry 9). Unfortunately, pivalic anhydride could not be employed as the substrate in the present catalytic system possibly because of its steric hindrance.

3. Palladium-catalyzed formal hydroacylation of allenes

As mentioned above, a hydrosilane is an excellent reducing reagent for the reduction of carboxylic anhydrides. Thus, the formal hydroacylation of cyclohexyllallene (**3a**) with **1a** was carried out using HSi^tPr₃ as a reducing agent in the presence of a catalytic amount of PdCl₂(MeCN)₂ in MeCN at 50 °C (Table 3). Under the reaction conditions, an *E/Z* mixture of hydroacylated product (**4a**) was obtained in 96% total yield with good *E*-selectivity (*E/Z*=88/12, entry 1). By column chromatography, pure (*E*)-**4a** was isolated in 71% yield. In this reaction, the addition of auxiliary ligands such as PPh₃ inhibited the formation of **4a** (entry 2). As for hydrosilane, HSiEt₃, HSiPh₃ and HSi(OEt)₃ were not effective (entries 3–5). PhCN as a solvent provided **4a** in 72%, while DMF and THF were not suitable for this reaction (entries 6–8).

Table 3
Optimization of reaction conditions on the palladium-catalyzed formal hydroacylation of cyclohexyllallene (**3a**) with **1a**^a



Entry	Hydrosilane	Solvent	Total yield (4a) (%) ^b	Selectivity (<i>E/Z</i>) ^c
1	HSi ^t Pr ₃	MeCN	96 (71) ^d	88/12
2 ^e	HSi ^t Pr ₃	MeCN	0	—
3	HSiEt ₃	MeCN	37	88/12
4	HSiPh ₃	MeCN	20	86/14
5	HSi(OEt) ₃	MeCN	39	78/22
6	HSi ^t Pr ₃	PhCN	81	89/11
7	HSi ^t Pr ₃	DMF	29	86/14
8	HSi ^t Pr ₃	THF	7	—

^a Reaction conditions: **1a** (0.50 mmol), cyclohexyllallene (**3a**: 1.0 mmol), hydrosilane (0.65 mmol), PdCl₂(MeCN)₂ (0.025 mmol, 5.0 mol %), solvent (1.0 mL) at 50 °C for 20 h.

^b Based on the GC internal standard technique.

^c Determined by GC and GC–MS analysis.

^d Isolated yield of (*E*)-**4a**.

^e PPh₃ (0.050 mol) was added.

Next, the formal hydroacylation of several allenes (**3**) with carboxylic anhydrides (**1**) was carried out under the same reaction conditions as in entry 1, Table 3 (Table 4). The reaction of **3a** with an aromatic carboxylic anhydride bearing electron withdrawing

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