



Facile Pd-catalyzed chemoselective transfer hydrogenation of olefins using formic acid in water



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ARTICLE INFO

Article history:

Received 1 July 2016

Revised 11 September 2016

Accepted 18 September 2016

Available online 19 September 2016

Keywords:

Transfer hydrogenation

Palladium

Chemoselective

Environmentally friendly catalyst

Water

ABSTRACT

An effective Pd-catalyzed reduction of olefins in water using formic acid is disclosed. A wide range of saturated hydrocarbons are obtained with an excellent conversion and remarkable chemoselectivity under mild reaction conditions. This protocol is more advantageous and less cumbersome owing to the use of HCOOH as a hydrogen source, water as a solvent, and simple workup procedure.

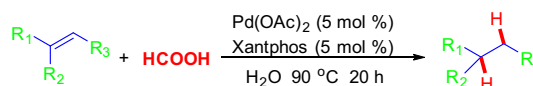
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Introduction

The chemoselective hydrogenation of double bond of olefins is a well-known protocol in organic chemistry, which has been used in the synthesis of pharmaceutical, fine chemicals, and functional materials.¹ While different approaches have been developed for the synthesis of this class of molecules, metal catalyzed transfer hydrogenations is most commonly used both in laboratory and in industry, which avoid some of the technical and safety concerns associated with using molecular hydrogen gas in the presence of Pd/C under high pressure and high temperatures.^{1,2} Several transition-metal catalyzed transfer hydrogenation with alcohol,³ amine,⁴ formate,⁵ and silicon hydride⁶ as the hydrogen donor has been continuously explored. Recently, a number of formic acid as an environmental-friendly hydrogen donor have been widely studied.⁷ In particular, Brunel⁸ reported work on a homogeneous catalytic palladium systems for chemoselective transfer hydrogenation using formic acid. Nevertheless, the functional group compatibility and low yields are still challenges. Therefore, the development of a very promising alternative method for effective transfer hydrogenation exhibiting the necessary selectivity and mildness is still desirable.⁹ Herein, we wish to report a simple, economical, and effective way to chemoselectively reduce the olefins in the presence of Pd catalyst using formic acid as hydrogen source in water (Scheme 1).

Results and discussion

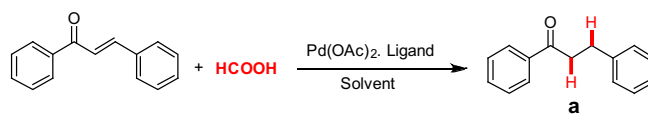
To explore the reaction conditions of the transfer hydrogenation reaction of olefins with formic acid as a hydrogen source, chalcone (**1a**) was selected as the test substrate and the results are listed in Table 1. For the optimization study, a range of ligands were initially examined. In the presence of the ligand such as PPh₃, dppe, dppp, dppb, and dppf, treating **1a** with HCOOH, and 5 mol % Pd(OAc)₂ in toluene at 90 °C for 20 h gave saturated ketone **2a** in low yield (Table 1, entries 1–5). Noteworthy, when the reaction was performed using bidentate ligand Xantphos (Table 1, entry 6), an increase in yield (92%) for the corresponding ketone **2a** was observed. The reduction was ineffective without any phosphorus ligands (Table 1, entry 7). Among the solvents examined to test the solvent effect, ethanol and water were found to be optimal for chemoselective transfer hydrogenation, giving the product **2a** in 99% yield (Table 1, entries 6, 8–13). However, water was selected as solvent, due to its being more environmentally friendly, and cheaper. The effects of various Pd catalysts were investigated, Pd(OAc)₂ has been proved more effective (Table 1, entries 12, 14, and 15). On decreasing the ratio of Pd(OAc)₂ and Xantphos, a poor



Scheme 1. Palladium-catalyzed transfer hydrogenation.

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Table 1
Studies of the reaction conditions^a

Entry	[Pd]	Ligand	Solvent	Yield ^b (%)
1	Pd(OAc) ₂	PPh ₃	Toluene	Trace
2	Pd(OAc) ₂	dppe	Toluene	72
3	Pd(OAc) ₂	dppp	Toluene	78
4	Pd(OAc) ₂	dppb	Toluene	81
5	Pd(OAc) ₂	dppf	Toluene	75
6	Pd(OAc) ₂	Xantphos	Toluene	92
7	Pd(OAc) ₂	—	Toluene	0
8	Pd(OAc) ₂	Xantphos	DMF	62
9	Pd(OAc) ₂	Xantphos	THF	71
10	Pd(OAc) ₂	Xantphos	DCM	78
11	Pd(OAc) ₂	Xantphos	Ethanol	99
12	Pd(OAc) ₂	Xantphos	Water	99
13	Pd(OAc) ₂	Xantphos	Dioxane	65
14	Pd(PPh ₃) ₄	Xantphos	Water	8
15	PdCl ₂	Xantphos	Water	43
16 ^c	Pd(OAc) ₂	Xantphos	Water	85
17 ^d	Pd(OAc) ₂	Xantphos	Water	88
18 ^e	Pd(OAc) ₂	Xantphos	Water	0
19 ^f	Pd(OAc) ₂	Xantphos	Water	72
20 ^g	Pd(OAc) ₂	Xantphos	Water	93
21 ^h	Pd(OAc) ₂	Xantphos	Water	58

^a The reactions were carried out with substrate **1a** (0.50 mmol), HCOOH (1.00 mmol), [Pd] (0.025 mmol), and ligand (0.025 mmol, P/Pd = 2:1) in toluene (0.50 mL) at 90 °C for 20 h unless otherwise stated.

^b Isolated yield.

^c With Pd(OAc)₂ (0.025 mmol) and Xantphos (0.050 mmol).

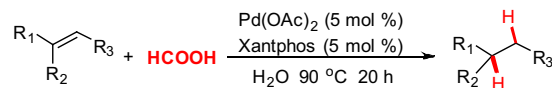
^d With Pd(OAc)₂ (0.020 mmol) and Xantphos (0.020 mmol).

^e The absence of HCOOH.

^f 1.0 equiv of HCOOH.

^g 3.0 equiv of HCOOH.

^h At 80 °C.

Table 2
Pd-catalyzed chemoselective transfer hydrogenation of olefins^a

Entry	Substrate	Product	Yield ^b (%)
1			99
2	X = <i>p</i> -H 1a	2a	99
3	X = <i>p</i> -Me 1b	2b	99
3	X = <i>p</i> -OMe 1c	2c	98
4			95
5	R = CH ₃ 1d	2d	95
6	R = H 1e	2e	96
7	R = OH 1f	2f	99
7	R = OMe 1g	2g	97
8			91
9	R = <i>p</i> -H 1i	2i	99
10	R = <i>p</i> -OMe 1j	2j	97
11	R = <i>p</i> -NH ₂ 1k	2k	91

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