



## Short Communication

## Iron oxide catalyzed reduction of acid chlorides to aldehydes with hydrosilanes



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## ABSTRACT

Iron-catalyzed reduction of acid chlorides to the corresponding aldehydes with a hydrosilane as a reducing agent has been developed. A simple mixture of a commercially available iron oxide (FeO) and tris(2,4,6-trimethoxyphenyl) phosphine (TMPP) as a catalyst realized the reduction of acid chlorides to the corresponding aldehydes under mild reaction conditions.

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## 1. Introduction

Acid chlorides are utilized as promising substrates in various organic reactions with transition-metal catalysts [1–5] because the oxidative addition of (acyl) carbon–chlorine bond to a low-valent metal center smoothly occurs [6]. Recently, we have reported iridium-catalyzed addition reaction of acid chlorides to terminal alkynes [7,8]. Importantly, aliphatic acid chlorides as well as aroyl chlorides could be used in the addition reaction with suppression of decarbonylation and  $\beta$ -hydrogen elimination which have been two major intrinsic problems in transition-metal-catalyzed reactions [8]. We also found the palladium-catalyzed reactions of acid chlorides with hydrosilanes in the presence of allenes, giving  $\alpha,\beta$ -unsaturated ketones regio- and stereoselectively [9].

The reduction of acid chlorides to aldehydes is one of the important methods to afford aldehydes. The transformation with molecular hydrogen over supported heterogeneous palladium catalysts (Pd/BaSO<sub>4</sub>) is well-known as the Rosenmund reduction [10]. However, in the reaction, the uptake of hydrogen must be monitored to avoid the over reduction. Homogeneous transition-metal catalyzed reductions of acid chlorides to the corresponding aldehydes have been also developed employing palladium [11] or ruthenium [12] as catalysts. Recently, we have reported a very efficient method of aldehydes synthesis from acid chlorides employing palladium catalysis and hydrosilane, which is stable, easy-to-handle and efficient reducing reagents [13]. Furthermore, we also developed the palladium-catalyzed reduction of carboxylic acids to the corresponding aldehydes in the presence of pivalic

anhydride and hydrosilane [14]. Although these were good catalytic reactions, complexes of precious metals such as ruthenium and palladium must be used.

Recently, much attention has been paid to iron catalysts since iron is one of the most abundant metals on the earth. Efficient iron-catalyzed transformations including carbon–carbon bond forming reactions have been developed to date [15–19]. Regarding iron-catalyzed reductive transformations [20–31], iron complexes were found to be active for reductions of carbonyl compounds such as aldehydes [20,21], ketones [20,21], and amides [22]. However, some iron complexes must be prepared before use and they might be unstable for further handling [20,21]. Therefore, iron-catalyzed transformation by the use of simple and commercially available catalyst precursors or in situ generated system is highly desired.

In the present study, we report that acid chlorides can be reduced to the corresponding aldehydes employing hydrosilane as a reducing agent in the presence of a catalytic amount of iron oxide (FeO) (99.9% purity). Iron oxides such as FeO or Fe<sub>2</sub>O<sub>3</sub> are known as catalysts in dehydrogenation reaction [32], Fenton reaction [33], or Fischer–Tropsch reaction [34]. However, to the best of our knowledge, there has been no precedent for the iron-catalyzed reduction of acid chlorides to aldehydes.

## 2. Experimental

## 2.1. General procedure

All manipulations were performed under an argon atmosphere using standard Schlenk-type glassware on a dual-manifold Schlenk

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**Table 1**  
Effect of iron precursors, ligands and hydrosilanes on the reduction of 3-phenylpropionyl chloride (**1a**).<sup>a</sup>

Entry	Fe precursor	Ligand	Hydrosilane	Conv. of <b>1a</b> (%) <sup>b</sup>	Yield of <b>2a</b> (%) <sup>b</sup>
1	FeO	TMPP	H <sub>3</sub> SiPh	93	57 (50) <sup>c</sup>
2	None	TMPP	H <sub>3</sub> SiPh	31	4
3	Fe <sub>2</sub> O <sub>3</sub>	TMPP	H <sub>3</sub> SiPh	83	43
4	FeCl <sub>2</sub>	TMPP	H <sub>3</sub> SiPh	26	2
5	FeF <sub>2</sub>	TMPP	H <sub>3</sub> SiPh	33	5
6	Fe(acac) <sub>2</sub>	TMPP	H <sub>3</sub> SiPh	53	3
7	FeO	None	H <sub>3</sub> SiPh	39	7
8	FeO	PPh <sub>3</sub>	H <sub>3</sub> SiPh	11	2
9	FeO	P[2,6-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>3</sub>	H <sub>3</sub> SiPh	32	15
10	FeO	P( <i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	H <sub>3</sub> SiPh	34	21
11	FeO	P( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	H <sub>3</sub> SiPh	91	28
12	FeO	P(Mes) <sub>3</sub>	H <sub>3</sub> SiPh	13	1
13	FeO	PCy <sub>3</sub>	H <sub>3</sub> SiPh	62	33
14	FeO	TMPP	HSiMePh <sub>2</sub>	24	5
15	FeO	TMPP	HSi(OEt) <sub>3</sub>	34	2
16	FeO	TMPP	H <sub>2</sub> SiMePh	42	14
17	FeO	TMPP	H <sub>2</sub> SiPh <sub>2</sub>	46	13
18	FeO	TMPP	PMHS	89	4

<sup>a</sup> Reaction conditions: Fe precursor(0.050 mmol, 20 mol%), ligand(0.013 mmol, 5.0 mol%) and hydrosilane(0.28 mmol) at 60 °C for 20 h, then, **1a** (0.25 mmol) and toluene (0.50 mL) at 60 °C for 20 h.

<sup>b</sup> Determined by GC analysis based on the internal standard technique.

<sup>c</sup> Isolated yield of **2a**.

line. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF and toluene were dried and purified before use by usual methods [35]. <sup>1</sup>H NMR spectra were measured with a JEOL ECX-400P spectrometer. The <sup>1</sup>H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The <sup>13</sup>C NMR chemical shifts are reported relative to CDCl<sub>3</sub> (77.0 ppm). GC analysis was carried out using Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-1, 0.25 mm i.d. × 25 m). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a SHIMADZU AXIMA-CFR Plus or a Bruker Autoflex using α-cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent. Medium-pressure column chromatography was performed with a Biotage IsoleraOne. Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63–210 μm). TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F254. Iron oxide (FeO, 99.9% purity) was purchased from Aldrich and used without further purification.

## 2.2. Catalytic reaction

A typical procedure for the iron oxide catalyzed reduction of 3-phenylpropionyl chloride (**1a**) with H<sub>3</sub>SiPh (Table 1, entry 1): iron oxide (3.6 mg, 0.050 mmol) and TMPP (6.7 mg, 0.013 mmol) were added to a 10 mL Schlenk flask with a magnetic stir bar. The flask was evacuated and backfilled with argon three times. Then, H<sub>3</sub>SiPh (34 μL, 0.28 mmol) was added to the flask and the reaction mixture was stirred at 60 °C for 20 h under an argon atmosphere. Then, toluene (0.50 mL) was added to the flask and the resultant solution was stirred at room temperature for 5 min before **1a** (37 μL, 0.25 mmol) was loaded. Further, the reaction mixture was stirred at 60 °C for 20 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with diethyl ether (5.0 mL) and tetradecane (50 μL, 0.19 mmol) as an internal standard was added. The yield of 3-phenylpropanal (**2a**; 57%) was analyzed by gas chromatography. **2a** was isolated by silica gel column chromatography (hexane: EtOAc = 13: 1). Pale yellow oil (16.8 mg) was obtained in 50% yield.

## 3. Results and discussion

To study activity of an iron catalyst system, we carried out reduction of 3-phenylpropionyl chloride (**1a**) as a model reaction. When all these materials including FeO, ligand, hydrosilane and **1a** were mixed all at once, **2a** was obtained only in moderate yields with poor reproducibility. Thus, a mixture of FeO, tris(2,4,6-trimethoxyphenyl)phosphine (TMPP), and H<sub>3</sub>SiPh was stirred at 60 °C for 20 h. Then, toluene and **1a** were added, and the resulting mixture was further stirred at 60 °C for 20 h. Under the reaction conditions, 3-phenylpropanal (**2a**) was obtained in 57% yield (entry 1). In the reaction mixture, 3-phenylpropionic acid was detected and its yield was determined as 32% by the GC internal standard method after derivatization to the corresponding methyl ester. This observation was in contrast to the palladium catalyzed reductions of acid chlorides [13], in which no carboxylic acids were formed. Without FeO, the conversion of **1a** was very low, and **2a** was obtained in only 4% yield (entry 2). Next, various iron precursors in place of FeO were employed. The reaction with Fe<sub>2</sub>O<sub>3</sub> also afforded **2a** in 43% yield (entry 3), while other soluble iron precursors such as FeCl<sub>2</sub>, FeF<sub>2</sub> and Fe(acac)<sub>2</sub> were not effective (entries 4–6). Without phosphine, the yield of **2a** considerably decreased (entry 7). Triphenylphosphine (PPh<sub>3</sub>) was not efficient at all (entry 8). The reaction employing triarylphosphines with electron donating substituents afforded **2a** in moderate yields (entries 9–11). Other bulky phosphines such as tris(2,4,6-trimethylphenyl)phosphine and tricyclohexylphosphine afforded the product in low yields (entries 12 and 13). Thus, the addition of a catalytic amount of a phosphine affects the activity considerably. As for a hydrosilane, HSiMePh<sub>2</sub>, HSi(OEt)<sub>3</sub>, H<sub>2</sub>SiMePh, H<sub>2</sub>SiPh<sub>2</sub>, and PMHS (polymethylhydrosiloxane) were less effective than H<sub>3</sub>SiPh (entries 14–18 vs entry 1). As a solvent, the reaction in THF under otherwise the same reaction conditions as entry 1 afforded **2a** in 40% yield. Regarding catalyst loadings, we carried out the reactions in the presence of 10 mol%, 5 mol%, and 1 mol% of FeO (the ratio of FeO:TMPP was kept in 4:1), and in these reactions **2a** was afforded in 49%, 19%, and 21% yields, respectively. In addition, the ratio between FeO and TMPP (4:1) was changed to 2:1, 1:1, and 1:2. As a result, the yield of **2a** was reduced to 50%, 40%, and 17% yields, respectively (Table S1, in the Supplementary data).

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