Communication

Efficient method for the reduction of carbonyl compounds by triethylsilane catalyzed by PdCl$_2$

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ABSTRACT

The versatility of the palladium(II) chloride and triethylsilane system has been tested in the reduction of aromatic carbonyl compounds. The reaction takes place under mild conditions. This facile and efficient method affords high yields for the reduction of aldehydes and ketones to the corresponding alkanes.

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1. Introduction

Hydrogenation of unsaturated organic functions such as olefins, carbonyls, and imines is currently becoming a standard procedure in both academic laboratories and industrial applications [1,2]. The development of a technique for the reduction of carbonyl compounds is very important [3]. Conventional hydrogenation procedure, although often offers reduction under mild conditions, requires a special set of apparatus and is always associated with the cautions of using hydrogen gas. Alternative methods to the commonly used hydrogenation procedures such as heterogeneous and homogeneous catalytic transfer hydrogenation have found widespread applications in the reduction of a large variety of functional groups [4–6]. Selective, mild and effective reducing agents in transition metal catalyzed transfer hydrogenation have been of considerable interest.

Transition metals such as Pd, Rh, Pt, Ni, Cu, Ir, Co and their complexes are usually utilized as catalysts for reduction reactions [7]. For example, ammonium formate/palladium on activated charcoal (Pd/C) system has shown its versatile catalytic hydrogen transfer and has been used for the reduction of various functionalities [8], including heterocyclic ring in quinolines [9], aryl ketones to alcohols [10], benzyl glycosides [11], dibenzyl uracils [12], α, β-unsaturated nitroalkenes [13] and cyclic α,β-unsaturated ketones [14]. Nickel(0) nanoparticles, generated from nickel(II) chloride, lithium

powder and a catalytic amount of 4,4-di-tert-buthylbiphenyl (DTBB) in THF at room temperature, were successfully used to promote the reduction of a variety of ketones and aldehydes by transfer hydrogenation using isopropanol as the hydrogen donor. Modest to high yields of the corresponding alcohols were obtained. However, the reduction of 4-methoxy benzaldehyde gave only 34% of the corresponding alcohol under the same conditions after 24 h [15]. On the other hand, good results have been obtained using poly[N-(2-aminoethyl)acrylamido]trimethyl ammonium halide resin with NaBH$_4$ [16]. Gamez et al. have described that the transesterification of several aromatic ketones including methyl phenylglyoxylate via hydride transfer using [Rh(C$_8$H$_{10}$)Cl]$_2$ as precursor, N,N-1,2-diphenyl-1,2-ethanediamine as ligand and isopropanol as the reducing agent and solvent, is faster than the reduction [17].

Trialkylsilanes are known to be poor reducing agents due to their low capacity to donate hydrogen atoms or hydrides [18]. To overcome these limitations, a variety of chemically modified silanes with weaker Si–H bonds and composite reducing systems based on the combination of a silane/transition-metal catalyst have been developed [19]. The combination of silicon hydride with palladium dichloride has been reported in few examples, i.e. for the deprotection of aminoacids or peptides [20], for nucleophilic substitution at silicon atom [21], for the reduction of Schiff bases [22], and for the preparation of halogenosilanes [23,24]. Furthermore, the system Et$_3$SiH/PdCl$_2$ was successfully used for the reduction of alkyl halides to alkanes [25], conversion of alcohols to their corresponding organic halides and alkanes [26], and for the effi-

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cient isomerization of 1-alkenes to 2- and 3-alkenes [27]. Moreover, the efficiency of the palladium catalyst/Et$_3$SiH system for the hydrogenation of 1-alkenes under mild conditions [28,29], for the transformation of alcohols to their corresponding silyl ethers and for the cleavage of triethylsilyl ethers to the parent alcohols [30] was demonstrated. More recently, we have shown the versatility of the PdCl$_2$/Et$_3$SiH system for the selective hydrogenation of the carbon–carbon double bond of α,β-unsaturated ketones to the corresponding saturated ketones under mild conditions [31].

This paper is a continuation of our previous work on the exploitation of Et$_3$SiH/PdCl$_2$ system for chemical transformation of organic functional groups. Herein, we report our preliminary results, which account for the versatility of PdCl$_2$/Et$_3$SiH couple in the chemical transformation of aromatic aldehydes and ketones to saturated compounds under mild conditions. Direct reaction of different aromatic aldehydes or ketones with Et$_3$SiH in the presence of palladium dichloride in ethanol occurs at room temperature to yield the corresponding saturated compounds in high yields. The reduction is most likely due to the reaction of the aldehydes or ketones with molecular hydrogen generated in situ by the spontaneous reaction of ethanol and triethylsilane catalyzed by palladium dichloride.

2. Results and discussion

The aim of the present work is exploring the efficiency of the system Et$_3$SiH/EtOH in the presence of catalytic amounts of PdCl$_2$ for the reduction of aromatic aldehydes and ketones under mild conditions (Scheme 1). The reduction reaction requires the use of an inert atmosphere and anhydrous solvent. In a typical experiment: PdCl$_2$ (10%) was added at room temperature to a stirred mixture of aldehyde or ketone (1 eq.) and Et$_3$SiH (2 eq.) in dry ethanol (2 ml). An exothermic reaction takes place in the first 5 min and then the temperature decreases to room temperature. The resulting mixture was further kept under stirring for indicated time in Table 1 prior to GC/MS analysis. The obtained results are summarized in Table 1.

First, the reaction of aromatic aldehydes and ketones with Et$_3$SiH/EtOH in the presence of PdCl$_2$ catalyst was examined at room temperature using the respective ratio 1/2/10 mol%. The results indicate that the reduction of aldehydes (entry 1–8) is high at room temperature in ethanol as solvent for an aldehyde/Et$_3$SiH = 1/2 ratio. However, we have observed the presence of the corresponding alcohol as intermediate in the reduction reaction. The reaction of benzyl alcohol with Et$_3$SiH/PdCl$_2$ system in presence of the solvent gave toluene after 30 min. It should be noted that for substrates with two unsaturated sites such as terephthaldehyde (entry 9), 4 eq. of triethylsilane were required to drive the reaction to completion. On the other hand, the reduction of 4-chlorobenzaldehyde
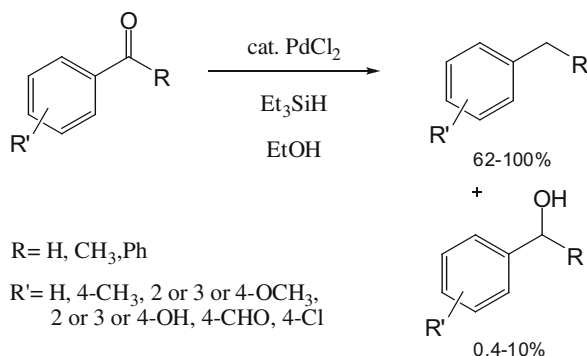
(entry 10) using aldehyde/Et$_3$SiH (1/2 ratio) yielded 62% of 4-chlorotoluene and 19% of toluene. There was a competition between the carbonyl and C–Cl reduction. The reduction of alkyl halides to the corresponding alkanes using Et$_3$SiH/PdCl$_2$ system was previously studied in detail [25]. When the ratio of aldehyde/Et$_3$SiH was increased from 1/2 to 1/6, the elimination of halide group increases to yield 44% of 4-chlorotoluene and 56% of toluene.

The reaction of acetophenone and 2-methoxyacetophenone (entries 11 and 12) with Et$_3$SiH (ketone/Et$_3$SiH: 1/2) produced respectively 73.5 and 88% of the saturated compound after 5 h reflux of ethanol. When the ratio of the ketone/Et$_3$SiH was increased to 1/4, ethylbenzene and 1-ethyl-2-methoxybenzene were obtained in 99 and 99.6% yields after only 1 h reflux of ethanol, respectively. In a similar way, the reaction of benzophenone (entry 13) with Et$_3$SiH in the presence of PdCl$_2$ led to the formation of diphenylmethane in 80% yield, after 30 min at room temperature. A yield of 100% was obtained when the ratio of benzophenone/Et$_3$SiH was increased to 1/6, after 30 min at room temperature.

We have next examined the reduction reaction of aliphatic ketones such as diisopropylketone, 5-nonanone and 2-heptanone using Et$_3$SiH/EtOH/PdCl$_2$. No reaction was observed after 6 h at room temperature or reflux in ethanol even in the presence of a large excess of Et$_3$SiH. Only the starting materials were recovered.

Finally, we have investigated the effect of the nature of the Pd catalyst ligand on the reduction reaction yield and product distribution. The reaction of 1 eq. of benzaldehyde with 2 eq. of Et$_3$SiH in the presence of 10% Pd(OAc)$_2$ as a catalyst led to the formation of 86.4% of benzyl alcohol and 13.6% of toluene after 50 min at room temperature in ethanol as solvent. The result is very different with that obtained using PdCl$_2$ as a catalyst (Table 1), and clearly indicates the role of the chloride on the product distribution.

Based on our previous reports [28,29,31], it is assumed that molecular hydrogen generated in situ by the reaction of Et$_3$SiH and ethanol in the presence of PdCl$_2$ is responsible of the reduction of the carbonyl group (Scheme 2).

The reaction of molecular hydrogen (H$_2$), generated by the reaction of Et$_3$SiH with EtOH catalyzed by Pd(0), with the carbonyl function leads to the formation of the corresponding alcohol. The transformation of alcohols to the corresponding halides and alkanes was previously studied in detail [25,26] and takes place according to Scheme 3.

To emphasize the role of the chloride ligand in the reaction mechanism, we have performed the reduction of benzyl alcohol by Et$_3$SiH/EtOH in the presence of catalytic amounts of PdCl$_2$ or Pd(OAc)$_2$. As discussed above, the reaction of benzyl alcohol with Et$_3$SiH (1/2) in the presence of 10% PdCl$_2$ gave 100% of toluene after 30 min at room temperature in ethanol as solvent. Under the same conditions, the use of Pd(OAc)$_2$ as a catalyst yielded only 18.5% of toluene and 81.5% of the starting alcohol. This clearly shows the influence of the chloride (or Et$_3$SiCl) on the reaction mechanism. However at this stage it is hard to draw a final conclusion regarding the exact reaction mechanism without performing more experiments.

In conclusion, we have developed a simple and highly efficient method for the reduction of carbonyl (C=O) group of aromatic aldehydes and ketones into –CH$_2$– group by the use of Et$_3$SiH in ethanol in the presence of PdCl$_2$ catalyst. The reaction is easy to carry out and takes place with high conversion yields.

3. Experimental

All manipulations were carried out under an argon atmosphere. The aldehydes, ketones and triethylsilane were obtained from Aldrich and used without further purification. Ethanol was distilled and stored under argon. GC/MS analysis was performed on a FISON
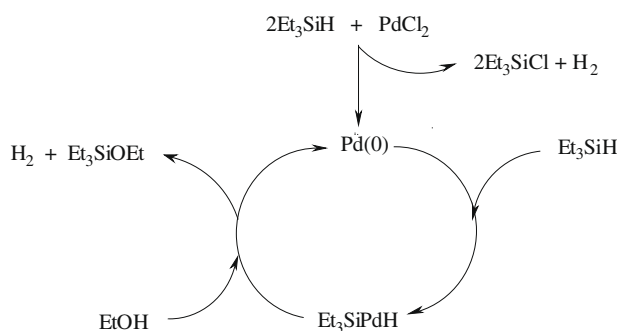
R= H, CH$_3$, Ph

R'= H, 4-CH$_3$, 2 or 3 or 4-OCH$_3$,
　　2 or 3 or 4-OH, 4-CHO, 4-Cl

Scheme 1.

Table 1
Reduction of aromatic aldehydes and ketones using $Et_3SiH/PdCl_2$ in ethanol

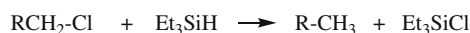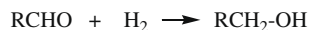| Entry	Substrate	Product	Substrate/Et$_3$SiH	Time (min)	Yield[a,b]%
1	Benzaldehyde	Toluene	1/2	30	95.5(4.5)
2	4-Methylbenzaldehyde	p-Xylene	1/2	30	88.5(10.0)
3	2-Methoxybenzaldehyde	2-Methylanisole	1/2	30	100.0
4	3-Methoxybenzaldehyde	3-Methylanisole	1/2	30	86.0
5	4-Methoxybenzaldehyde	4-Methylanisole	1/2	30	100.0
6	2-Hydroxybenzaldehyde	o-Cresol	1/2	30	94.5(2.0)
7	3-Hydroxybenzaldehyde	m-Cresol	1/2	30	92.0(6.5)
8	4-Hydroxybenzaldehyde	p-Cresol	1/2	30	98.0(2.0)
9	Terephthaldehyde	p-Xylene	1/4	30	100.0
10	4-Chlorobenzaldehyde	4-Chlorotoluene	1/2	30	62.0[c]
11	Acetophenone	Ethylbenzene	1/4	30	99(1.0)
12	2-Methoxyacetophenone	1-Ethyl-2-methoxybenzene	1/4	60(reflux)	99.6(0.4)
13	Benzophenone	Diphenylmethane	1/4	60(reflux)	100.0

[a] Determined by GC/Ms analysis.
[b] The number between the parentheses show the percent of the corresponding alcohol.
[c] The reduction of 4-chlorobenzaldehyde gave 62% of 4-chlorotoluene and 19% of toluene.

$$2Et_3SiH + PdCl_2$$

$$\longrightarrow 2Et_3SiCl + H_2$$

$$H_2 + Et_3SiOEt$$

$$Pd(0)$$

$$Et_3SiH$$

$$EtOH$$

$$Et_3SiPdH$$

Scheme 2.

$$RCHO + H_2 \longrightarrow RCH_2\text{-}OH$$

$$RCH_2\text{-}OH + Et_3SiCl \longrightarrow RCH_2\text{-}Cl$$

$$RCH_2\text{-}Cl + Et_3SiH \longrightarrow R\text{-}CH_3 + Et_3SiCl$$

Scheme 3.

GC 8000 series TRIO 1000 gas chromatograph equipped with a capillary column CP Sil.5 CB, 60 M × 0.25 mm Id. ^{1}H NMR spectra were recorded on a Bruker 80 or 500 spectrometer using TMS as internal standard.

4. General procedure for reduction of carbonyl compounds

To a solution of carbonyl compounds (0.2 g, 1 eq.) and triethylsilane (amount indicated in Table 1) in 5 ml of ethanol was added a catalytic amount of palladium(II) chloride (10 mol%) under an argon atmosphere. The resulting mixture was kept under stirring for the time indicated in Table 1 prior to GC/MS analysis. The pure products for entry 1–2 and 9–11 were isolated by distillation and for entry 3–8 and 12–13 were isolated by column chromatography using hexane/ethylacetate (9/1) as eluent. The products were characterized using ^{1}H NMR and mass spectrometry. Spectroscopic data for selected compounds:

Entry 3, Table 1, ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 2.25 (s, 3H, CH$_3$), 3.83 (s, 3H, OCH$_3$), 6.77–7.18 (m, 4H, CH arom.). MS (70 eV), m/z (%): 122 (100) (M$^+$), 107 (62), 91 (50), 77 (56).

Entry 5, Table 1, ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 2.33 (s, 3H, CH$_3$), 3.83 (s, 3H, OCH$_3$), 6.85 (d, J = 8.60 Hz, 2H, CH arom.), 7.13 (d, J = 8.6 Hz, 2H, CH arom.). MS (70 eV), m/z (%): 122 (100) (M$^+$), 107 (45), 91 (30), 77 (62).

Entry 7, Table 1, ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 2.36 (s, 3H, CH$_3$), 5.24 (s, 1H, OH), 6.69 (m, 2H, CH arom.), 6.80 (d, J = 7.73 Hz, 1H, CH arom.), 7.18 (t, J = 7.73 Hz, 1H, CH arom.). MS (70 eV), m/z (%):108 (90) (M$^+$), 107 (100), 79 (45).

Entry 8, Table 1, ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 2.21 (s, 3H, CH$_3$), 4.43 (s, 1H, OH), 6.64 (d, J = 8.60 Hz, 2H, CH arom.), 6.97 (d, J = 8.60 Hz, 2H, CH arom.). MS (70 eV), m/z (%): 108 (75) (M$^+$), 107 (100), 77 (40).

Entry 12, Table 1, ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 1.37 (t, J = 7.53 Hz, 3H, CH$_3$), 2.81 (q, J = 7.53 Hz, 2H, CH$_2$), 3.96 (s, 3H, OCH$_3$), 6.98 (d, J = 7.50 Hz, 2H, CH arom.), 7.05 (t, J = 7.50 Hz, 1H, CH arom.), 7.34 (m, 2H, CH arom.). MS (70 eV), m/z (%): 136 (56) (M$^+$), 121 (100), 91 (50), 77 (12).

Entry 13, Table 1, ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 4.03 (s, 2H, CH$_2$), 7.17 (s, 10H, CH arom.). MS (70 eV), m/z (%): 168 (87) (M$^+$), 167 (100), 153 (25), 91 (22).

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