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Communication

Palladium catalyzed mild reduction of α,β-unsaturated compounds by triethylsilane

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Abstract

The palladium(II) chloride/triethylsilane system has been successfully applied for the selective hydrogenation of the carbon–carbon double bond of α,β-unsaturated ketones to yield the corresponding saturated carbonyl compounds. The reaction takes place under mild conditions and affords high yields.

Keywords: Palladium(II) chloride; Triethylsilane; Hydrogenation; α,β-Unsaturated ketones

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]. Though reduction of an isolated functional group can be carried out conveniently with a number of reagents, selective reduction of one functionality in the presence of other functional groups with a minimum damage to the sensitive portion of a molecule is a frequent problem in organic synthesis. Thus, the development of a technique for the selective hydrogenation of C=C double bond of conjugated carbonyl compounds in the presence of other isolated double bonds is very important, but remains difficult [3]. Conventional hydrogenation procedure, although often offers selective 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]. Transition metals such as Pd, Rh, Pt, Ni, Cu, Ir, Co and their complexes are usually utilized as catalysts for reduction reaction [7]. For example, ammonium formate/palladium on activated charcoal 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]. On the other hand, palladium complex, $[(t\text{-}Bu_2PH)Pd\ (P\text{-}t\text{-}Bu_2)]_2$ was found efficient catalyst for the selective hydrogenation of the carbon–carbon double bond of α,β-unsaturated ketones, aldehydes, sulfones and phosphonates in good to excellent yields [15,16]. The selective transfer hydrogenation of α,β-unsaturated carbonyl compounds to saturated ones was achieved by the use of 2-propanol as a hydrogen donor under the influence of catalytic amounts of $[Ir(cod)Cl]_2$, 1,3-bis(diphenylphosphino)propane and Cs_2CO_3 [17]. Good results

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have also been obtained using $(Cy_3P)_2Rh(H)(Cl)_2$ under biphasic conditions [18]. A combination of $InCl_3$ and Me_3SiCl was successfully used to promote the reduction of α,β-unsaturated ketone to the corresponding ketone in the presence of triethylsilane [19].

Trialkylsilanes are known to be poor reducing agents due to their low capacity to donate hydrogen atoms or hydrides [20]. 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 [21]. The combination of silicon hydrides with palladium dichloride has been reported in few examples, i.e., for the deprotection of aminoacids or peptides [22], for nucleophilic substitutions at silicon atom [23], for the reduction of Schiff bases [24], and for the preparation of halosilanes [25–27]. Furthermore, the system $Et_3SiH/PdCl_2$ was successfully applied for the conversion of organic halides to the corresponding alkanes [28] and for the transformation of alcohols to their corresponding halides and alkanes [29]. More recently, we have demonstrated the high efficiency of $PdCl_2$ and triethylsilane for the carbon–carbon double bond isomerization of 1-alkenes to yield the corresponding 2- and 3-alkenes [30] and for the reduction of alkenes to the corresponding alkanes [31] in the presence of ethanol as solvent, at room temperature.

Herein we report our preliminary results, which account for the versatility of the $PdCl_2/Et_3SiH$ system for the selective hydrogenation of the carbon–carbon double bond of α,β-unsaturated ketones to the corresponding saturated ketones under mild conditions. The present work was aimed at exploring the efficiency of molecular hydrogen generated in situ by the reaction of Et_3SiH with EtOH in the presence of catalytic amounts of $PdCl_2$ for the selective reduction of the carbon–carbon double bond of α,β-unsaturated carbonyl compounds (Scheme 1).

The hydrogenation reaction requires the use of an inert atmosphere and anhydrous solvent. In a typical experiment, palladium dichloride (10 mol%) was added at room temperature to a stirred mixture of α,β-unsaturated ketone (1 equiv) and Et_3SiH (2 equiv) in dry ethanol (10 ml). An exothermic reaction takes place in the first 5 min and then the temperature decreases to room temperature. The resulting mixture was then stirred for 2 days at room temperature or refluxed for 6 h prior to GC/MS analysis. These conditions were applied with success to α,β-unsaturated ketones and the results are listed in Table 1.

First, the reaction of α,β-unsaturated ketones with Et_3SiH/EtOH in the presence of $PdCl_2$ catalyst was examined at room temperature. The reduction of the carbon–carbon double bond takes place quantitatively. For example, the reaction of 1 equiv of 2-cyclohexene-1-one or mesityl oxide with $Et_3SiH/PdCl_2$ (2 equiv/10%) in 10 ml of ethanol for 2 days at room temperature led to the formation of 99% of cyclohexenone and 97% of 4-methyl-2-pentanone, respectively.

Under the same conditions, isophorone gave 92% of the saturated ketone. However, the substrate with two unsaturated sites as phorone, 4 equiv of triethylsilane are required to drive the reaction to completion (Table 1, entry 4). Chalcone and benzalacetone were also hydrogenated in good yields.

The effect of the temperature on the conversion yield was examined. High yields (93–100%) were obtained when the temperature of the reaction was increased to the reflux of ethanol after only 6 h.

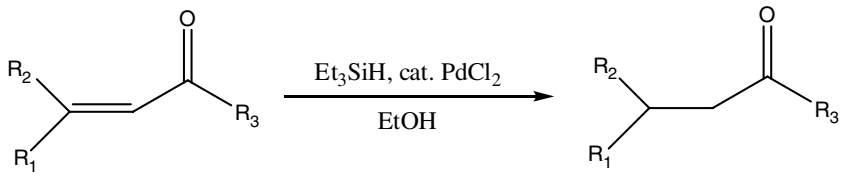
The hydrogenation reaction is believed to occur by addition of molecular hydrogen, generated by the reaction of Et_3SiH with ethanol catalyzed by Pd species, to the unsaturated functional groups (C=C groups) (Scheme 2).

This assumption is made based on our previous reports [29,31,32]. We found that molecular hydrogen can be generated by the reaction of ethanol with triethylsilane in the presence of $PdCl_2$ catalyst. The as-formed hydrogen reacts efficiently with the carbon–carbon double bond of simple alkenes to yield the corresponding alkanes in high yields [31,32]. In the present work, we do believe that the reduction of the C=C double bond takes place in a similar reaction pathway.

In conclusion, we have developed a simple and highly efficient method for selective reduction of carbon–carbon double bond of α,β-unsaturated ketones by the use of excess Et_3SiH in ethanol in the presence of $PdCl_2$ catalyst. The reaction is easy to carry out and takes place with high conversion yields. The reaction is believed to occur by selective addition of molecular hydrogen, generated in situ, on the carbon–carbon double bond. However without any further experimental details, it is hard to draw any conclusion regarding the observed reaction pathway.

2. Experimental

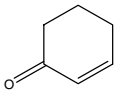
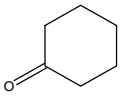
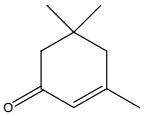
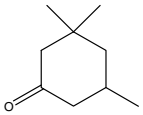
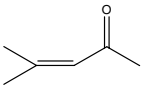
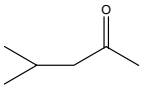
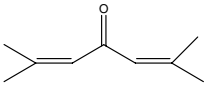
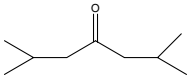
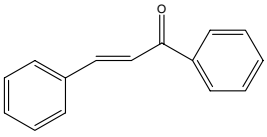
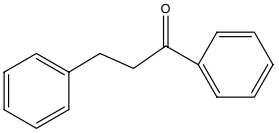
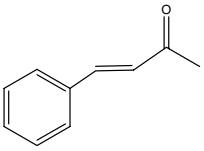
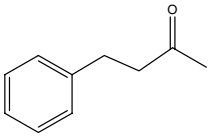
All manipulations were carried out under an argon atmosphere. The α,β-unsaturated ketones and triethylsilane



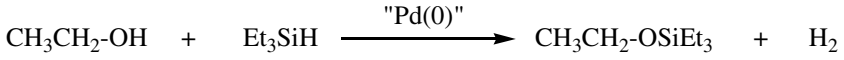
1a-f **2a-f**

Scheme 1.

Table 1
Selective reduction of the carbon–carbon double bond of α,β-unsaturated ketones using $Et_3SiH/PdCl_2$: 2/0.1 in ethanol

Entry	Substrate	Product	Yield[a] (%)
1	 **1a**	 **2a**	**95**
2	 **1b**	 **2b**	**93**
3	 **1c**	 **2c**	**95**
4	 **1d**	 **2d**	**90**[b]
5	 **1e**	 **2e**	**87**
6	 **1f**	 **2f**	**85**

[a] Isolated yields.
[b] 4 equiv of Et_3SiH are used.



Scheme 2.

were obtained from Aldrich and used without further purification. Ethanol was distilled and stored under argon. GC/MS analysis was performed on a FISON 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.

2.1. General procedure for reduction of α,β-unsaturated carbonyl compounds

To a solution of α,β-unsaturated carbonyl compounds (0.2 g, 1 equiv) and triethylsilane (2 equiv) in 10 ml of ethanol was added a catalytic amount of palladium(II) chloride (10 mol%) under an argon atmosphere. The resulting mixture was refluxed for 6 h prior to GC/MS analysis. The pure products **2b**, **2e** and **2f** were isolated by column chromatography using hexane/ethyl acetate (9/1) as eluent while the compounds **2a**, **2c** and **2d** were isolated by distillation. The products were characterized using ^{1}H NMR and mass spectrometry. Spectroscopic data for **2a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.75 (m, 2H), 1.89 (m, 4H), 2.35 (t, $J = 6.7$ Hz, 4H), MS (m/z): 98 (M^+, 97), 83, 80, 70, 69, 55 (100). Compound **2b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.89 (s, 3H), 1.02 (d, $J = 6.4$ Hz, 3H), 1.06 (s, 3H), 1.31 (t, $J = 12.8$ Hz, 1H) 1.60 (m, 1H), 1.89 (t,

$J = 12.6$ Hz, 1H), 2.04 (m, 2H), 2.16 (d, $J = 13.3$ Hz, 1H), 2.32 (m, 1H), MS (m/z): 140 (M^+, 42), 125, 97, 84, 83, 69, 55 (100). Compound **2c**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.97 (d, $J = 7.7$ Hz, 6H), 2.16 (s, 3H), 2.17 (m, 1H), 2.34 (d, $J = 7.2$ Hz, 2H), MS (m/z): 100 (M^+, 25), 85 (100), 67, 58, 57. Compound **2d**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.93 (d, $J = 6.6$ Hz, 12H), 2.16 (m, 2H), 2.27 (d, $J = 6.9$ Hz, 4H), MS (m/z): 142 (M^+, 20), 127, 100, 86, 85, 58, 57 (100). Compound **2e**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ: 3.19 (m, 4H), 7.18–7.94 (m, 10), MS (m/z): 210 (M^+, 50), 105, 91, 77 (100), 51. Compound **2f**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ: 2.06 (s, 3H), 2.75 (m, 4H), 7.11–7.22 (m, 5H), MS (m/z): 148 (M^+, 95), 133, 105, 91, 77, 51, 43 (100).

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