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Palladium-catalyzed reduction of olefins with triethylsilane

Maryam Mirza-Aghayan,^{a,*} Rabah Boukherroub,^b Mohammad Bolourtchian^a and Maryam Hosseini^a^aChemistry and Chemical Engineering Research Center of Iran (CCERC), PO Box 14335-186, Tehran, Iran^bPhysique de la Matière Condensée, Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France

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Abstract—The versatility of the palladium(II) chloride and triethylsilane system has been tested in the hydrogenation of 1-alkenes. The reduction of 1-alkenes was carried out in the presence of triethylsilane, ethanol and a catalytic amount of palladium(II) chloride, at room temperature. This facile and efficient method affords high yields for hydrogenation of unsaturated alkenes to the corresponding alkanes. © 2003 Elsevier Science Ltd. All rights reserved.

Hydrogenation of unsaturated compounds is one of the most important reactions in organic chemistry and hence several reagents have been utilized for this purpose.¹ The addition of hydrogen to an alkene to form the corresponding alkane is highly favored thermodynamically. However, the reaction rate is negligible under ordinary conditions in the absence of a catalyst. Selective, mild and effective reducing agents in transition metal-catalyzed transfer hydrogenation have been of considerable interest.

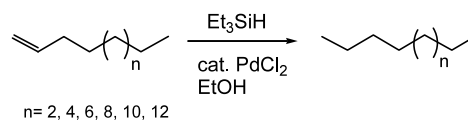
Trialkylsilanes are known to be poor reducing agents, due to their low capacity to donate hydrogen atoms or hydrides.² To overcome these limitations, a variety of modified silanes with weaker Si–H bonds and composite reducing systems based on a combination of a silane/transition-metal catalyst have been developed.³ Earlier work by Kursanov et al.⁴ described ionic hydrogenation of carbon–carbon double bonds and carbonyl compounds using triethylsilane and an excess of trifluoroacetic acid. Moreover, Lipowitz and Bowman⁵ have used polymethylhydrosiloxane (PMHS) and a palladium-on-charcoal catalyst for hydrogenating 1-alkenes in high yields at 40–60°C. However, the reaction of 2-nonene gave only 25% of the corresponding *n*-nonane under the same conditions.

More recently, palladium dichloride was used as the catalyst for the conversion of organic halides to the corresponding alkanes by triethylsilane at room temperature in high yields.⁶ The versatility of the system

Et₃SiH/PdCl₂ was demonstrated for the conversion of alcohols to their corresponding silyl ethers, halides and alkanes,⁷ and for the efficient isomerization of 1-alkenes to 2- and 3-alkenes.⁸

The present work was aimed at exploring the efficiency of the system Et₃SiH/EtOH in the presence of catalytic amounts of PdCl₂ for hydrogenation of 1-alkenes under mild conditions (Scheme 1). The hydrogenation reaction requires the use of an inert atmosphere and anhydrous solvent. In a typical experiment: palladium dichloride (10%) was added at room temperature to a stirred mixture of the 1-olefin (1 equiv.) and Et₃SiH (2 equiv.) in dry ethanol (2 ml). An exothermic reaction took place in the first 5 min. and then the temperature decreased to room temperature. The resulting mixture was then stirred for 15 h at room temperature prior to GC/MS analysis. The results obtained are summarized in Table 1.

We tried different experimental conditions in order to optimize the conversion of the 1-alkene to the corresponding alkane. We found that the reaction of 1 equiv. of 1-dodecene with Et₃SiH/PdCl₂ (0.5 equiv./10%) for 17 h at room temperature led to a lower yield of *n*-dodecane (35%). Increasing the amount of Et₃SiH in the reaction mixture (Et₃SiH/PdCl₂: 2 equiv./10%) increased the conversion and the yield of *n*-dodecane to

**Scheme 1.**

Keywords: hydrogenation; 1-alkenes; palladium(II) chloride; triethylsilane; ethanol.

* Corresponding author. Tel.: +98 21 8036144-5; fax: +98 21 8037185.

Table 1. Reduction of 1-alkenes using Et₃SiH/PdCl₂: 2/0.1 in ethanol as solvent

Entry	Time (days)	% Yield ^a
1-Octene	1	100
1-Decene	1	90
1-Dodecene	1.5	97
1-Tetradecene	1	73
1-Hexadecene	1.5	97
1-Octadecene	1	96

^a Determined by GC/MS analysis.

73% (24% isomerized dodecenes were obtained). The reaction time also has an influence on the product distribution. The reaction of 1 equiv. of 1-dodecene with Et₃SiH/PdCl₂ (2 equiv./10%) for 1.5 days at room temperature yielded 97% of *n*-dodecane. However, three days were required to obtain a 92% conversion of 1-tetradecene to *n*-tetradecane.

In summary, this work demonstrates high efficiency for reduction of alkenes to the corresponding alkanes using PdCl₂, triethylsilane and ethanol as solvent, at room temperature. It should be noted that no hydrosilylation reaction took place during the hydrogenation process and only the corresponding alkanes were obtained in high yields.

Experimental

All manipulations were carried out under an argon atmosphere. Ethanol was distilled and stored under argon. Yields are based on GC/MS analysis using a FISON GC 8000 series TRIO 1000 gas chromatograph equipped with a capillary column CP Sil.5 CB, 60 M×0.25 mm Id.

General procedure for reduction of α -olefins

To a solution of 1-alkene (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 stirred for 15 h or 1.5 days at room temperature prior to GC/MS analysis.

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