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A mild and efficient palladium–triethylsilane system for reduction of olefins and carbon–carbon double bond isomerization

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The versatility of palladium(II) acetate and palladium on activated charcoal catalysts with triethylsilane has been investigated in the hydrogenation and the isomerization of carbon–carbon double bond of 1-alkenes. The reduction of 1-alkenes was carried out in the presence of triethylsilane, ethanol and a catalytic amount of palladium(II) acetate or palladium on activated charcoal, at room temperature. This facile and efficient method affords high yields for hydrogenation of unsaturated alkenes to the corresponding alkanes. Then the carbon–carbon double bond isomerization of 1-alkenes was tested using the same catalysts in the absence of solvent. The system palladium(II) acetate-triethylsilane was found to be more effective compared with palladium on an activated charcoal–triethylsilane system at room temperature, while comparable results were obtained at 50 °C for both catalysts. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: reduction; isomerization; 1-alkenes; palladium(II) acetate; palladium on activated charcoal; triethylsilane

INTRODUCTION

Hydrogenation and isomerization of the carbon–carbon double bond of an unsaturated compound are the most important reactions in organic chemistry. Selective, mild and effective reducing agents in transition metal catalyzed transfer hydrogenation have been used for this purpose.[1–7]

Olefin isomerization occurs to a large extent in petrochemical refining processes (heterogeneous catalysis) and follows the thermodynamic driving forces. Transition metal-catalyzed olefin isomerization has been an area of considerable interest. Diverse processes for olefin isomerization continue to be topics of widespread interest.[8–16] Transition metals such as rhodium and nickel facilitate the attainment of the thermodynamic equilibrium under mild conditions, often at room temperature.[17] The isomerization of 1-heptene in the presence of $Ni[P(OEt)_3]_4$ has been reported. The reaction was initiated by adding H_2SO_4 to an ether solution of 1-heptene and $Ni[P(OEt)_3]_4$ at 0 °C.[18] However, the nickel catalyst is not very stable in air and thus requires special care during its transfer and manipulation. Another example of an isomerization process consisting of contacting olefins with a titanium catalyst on alumina in the presence of water takes place at 300–570 °C.[13]

Silicon hydrides have met successful applications in substitution, reduction and addition processes.[19–22] Synthetic applications of silicon hydrides with palladium(II) have already been reported for the reduction of Schiff-bases,[23] the preparation of halosilanes,[24,25] nucleophilic substitutions at silicon atom,[26,27] and for the deprotection of aminoacids or peptides.[28,29] Ionic hydrogenation of carbon–carbon double bonds and carbonyl compounds using triethylsilane and an excess of trifluoroacetic acid has been described.[30] Polymethylhydrosiloxane (PMHS) and palladium-on-charcoal catalyst have been used for hydrogenating 1-alkenes in high yields.[31] However, the reaction of 2-nonene gave only 25% of the corresponding *n*-nonane under the reported conditions.

In our previous studies, we have investigated the system $Et_3SiH–PdCl_2$ for various chemical transformations under mild conditions. It was successfully applied for the conversion of organic halides to the corresponding alkanes[32] and for the conversion of alcohols to their corresponding halides and

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alkanes.[33] The versatility of the system $Et_3SiH–PdCl_2$ was also demonstrated for the reduction of olefins to alkanes,[34] conversion of alcohols to their corresponding silyl ethers and cleavage of the triethylsilyl ethers to the parent alcohols,[35] and for the efficient isomerization of 1-alkenes to 2- and 3-alkenes.[36]

In earlier studies on the isomerization of 1-alkenes with $Et_3SiH–PdCl_2$, we have observed molecular hydrogen formation along with metallic Pd. We have proposed a mechanism in which metallic Pd(0) is believed to serve as the active entity in the catalyzed isomerization reaction and account for the formation of the corresponding alkanes.[34,36]

This paper is an extension of our previous work on the exploitation of $Et_3SiH–PdCl_2$ system for chemical transformation with the aim to generalize the technique for other palladium-based catalysts. We have investigated palladium on activated charcoal (Pd–C)–Et_3SiH and palladium(II) acetate [$Pd(OAc)_2$]–Et_3SiH systems in the reduction of 1-alkenes to the corresponding alkanes and olefin isomerization under mild conditions. Direct reaction of ethanolic solution of different olefins with triethylsilane in the presence of commercially available 10 mol% Pd–C or $Pd(OAc)_2$ occurs at room temperature to yield the corresponding alkanes in high yields. The obtained results are comparable to the previously reported for $Et_3SiH–PdCl_2$ under the same conditions. The second aspect of this work consists of the isomerization of 1-alkenes to the corresponding 2- and 3-isomers using triethylsilane and catalytic amounts of Pd–C or $Pd(OAc)_2$. It was found that the isomerization reaction using palladium(II) catalysts–Et_3SiH gave comparable results and yields, while Pd–C catalyst offered lower yields. However, high isomerization conversion yields were obtained when the reaction was conducted at 50 °C.

RESULTS AND DISCUSSION

Hydrogenation

The following procedure was used to prepare the desired product: addition at room temperature of 10 mol% Pd–C or $Pd(OAc)_2$ to a stirred mixture of olefin (1 equiv.) and triethylsilane (2 equiv.) in the presence of ethanol as solvent gave the corresponding alkane in good yield (Scheme 1).

The hydrogenation reaction was carried out under a controlled atmosphere in anhydrous solvent. An exothermic reaction took place following the addition of 10 mol% Pd-based catalysts to a stirred mixture of 1-olefin, Et_3SiH and EtOH. The temperature decreased to room temperature after 5 min and the mixture was kept under stirring for 24 h. The results are summarized in Table 1. The two catalysts are highly efficient and 10 mol% was sufficient to promote reduction of the alkenes.

The hydrogenation reaction takes place by addition of molecular hydrogen (generated by the reaction of Et_3SiH with ethanol catalyzed by Pd species) to the C=C double bond. The proposed reaction mechanism is corroborated by several experimental facts. First, during the dehalogenation reaction of alkyl or aryl halides [equation (1)], we have identified using GC/MS the presence of small amounts of Et_3SiCl along the corresponding silyl halide, independently of the starting halide.[32] The presence of Et_3SiCl may account for a complex process (oxidative addition followed by a reductive elimination) during the reaction. It is believed that the active catalyst species during the reaction is the Pd(0) generated *in situ* according to equation (2).

$$R'\text{-}X + R_3Si\text{-}H \longrightarrow R'\text{-}H + R_3Si\text{-}X \quad (1)$$

$$2\,Et_3Si\text{-}H + PdCl_2 \longrightarrow 2\,Et_3Si\text{-}Cl + Pd(0) + H_2 \quad (2)$$

Moreover, we have shown that alcohols can be easily transformed to their corresponding silylethers by the reaction with $Et_3SiH–PdCl_2$.[35] The side product of the reaction is molecular hydrogen [equation (3)]:

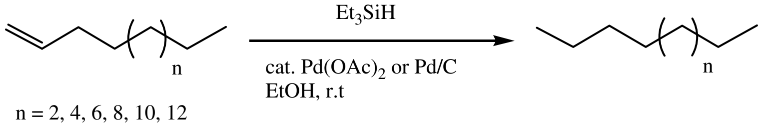
$$RCH_2\text{-}OH + R'_3SiH \xrightarrow{\text{cat. }PdCl_2} RCH_2\text{-}OSiR'_3 + H_2 \quad (3)$$

Based on the above observations, we do believe that the reaction mechanism for the hydrogenation of olefins catalyzed by Pd-based species is a stepwise process. For

Table 1. Hydrogenation of 1-alkenes using $Et_3SiH–Pd(OAc)_2$ or Pd–C 2 : 0.1 in 10 ml ethanol as solvent after 1 day reaction at room temperature

Entry	% Alkane[a] [using $Pd(OAc)_2$]	Alkane[a] (%) (using Pd–C)
1-Octene	100	100
1-Decene	98	91
1-Dodecene	90	90
1-Tetradecene	98	100
1-Hexadecene	98	95
1-Octadecene	100	100

[a] Conversions determined by GC/MS analysis.



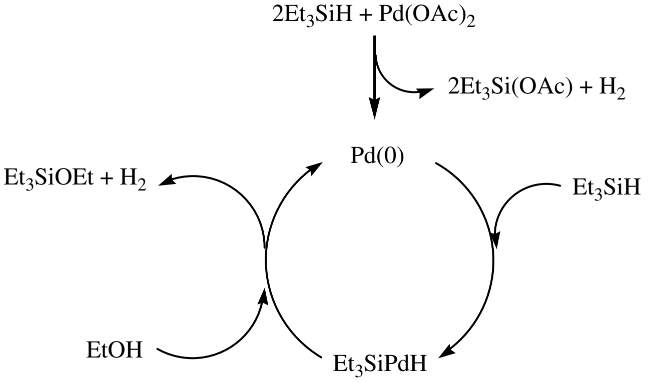
Scheme 1.

the $Pd(OAc)_2$–Et_3SiH system, the first step corresponds to the reaction of palladium acetate with Et_3SiH leading to the formation of active metallic Pd(0) entity in the catalyzed reaction[25,33] (Scheme 2). Oxidative addition of Et_3SiH to Pd(0) leads to the formation of Et_3SiPdH complex, which can be displaced by ethanol to generate molecular hydrogen and triethylsilyl ether accompanied by the regeneration of the Pd catalyst. The generated molecular hydrogen may adsorb on the metallic palladium and add to the C=C double bond to form the corresponding alkane.[34]

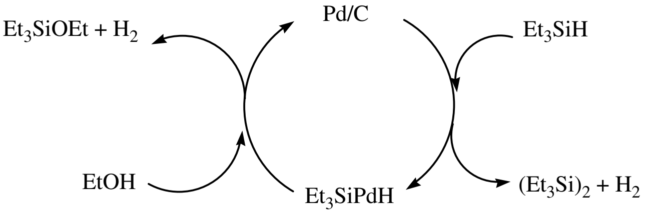
In the case of the Pd–C–Et_3SiH system, the reaction mechanism is similar to the previous one with the difference that the palladium is already in its reduced form. The generation of molecular hydrogen may occur by oxidative addition of Et_3SiH to the metallic Pd, followed by reaction with ethanol (Scheme 3).

Isomerization

In the second step we investigated the isomerization of 1-olefins using the same catalysts. The isomerization reaction also requires the use of an inert atmosphere. Initially, we carried out the reaction at room temperature. In a typical experiment, palladium catalyst (10 mol%) was added at room temperature to a stirred mixture of 1-alkene (1 equiv.) and Et_3SiH (1 equiv.). An exothermic reaction took place in the first 5 min and then the temperature decreased to room temperature. The resulting mixture was kept under stirring for 17 and 6 h at room temperature for Pd–C and $Pd(OAc)_2$, respectively, prior to GC/MS analysis. The isomerization of 1-olefins is outlined in Scheme 4.



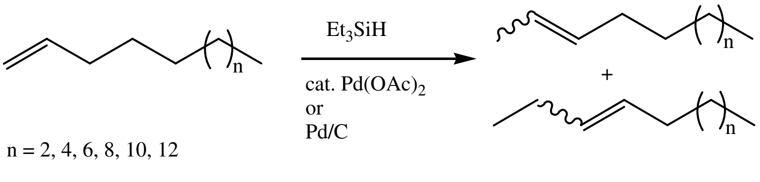
Scheme 2.



Scheme 3.

The results obtained are summarized in Tables 2 and 3. GC/MS analysis of the crude mixture resulting from the reaction of 1-alkene with Et_3SiH in the presence of Pd–C shows the formation of isomers 2-alkene and 3-alkene (*cis*/*trans* mixtures) along with the starting 1-alkene and the corresponding alkane (Table 2). There was no formation of other products resulting from additional isomerization of the C=C double bond or from hydrosilylation reaction, even for longer reaction times. The yields were satisfactory for C=C double bond isomerization of 1-octene, 1-decene and 1-octadecene (67, 69 and 67%, respectively), but a modest conversion yield was observed for 1-dodecene, 1-tetradecene and 1-hexadecene. Next, we investigated the effect of temperature and reaction time on the isomerization reaction. We found that both parameters influence the product distribution and conversion. When the isomerization reaction was carried out at 50 °C for 6 h, the conversion yield for 1-dodecene, 1-tetradecene and 1-hexadecene increased from 33, 28 and 26% to 42, 57 and 44%, respectively. Increasing the reaction time from 6 to 10 h, while maintaining the temperature constant, led to the improvement of the conversion yield by a factor 2. For example, the reaction of 1-tetradecene with Et_3SiH–Pd–C at room temperature led to the formation of 1-tetradecene–2-tetradecene–3-tetradecene–tetradecane (57–16–12–14) mixture in 28% yield. The same reaction carried out at 50 °C for 10 h gave a ratio of 34–38–22–6 in 60%.

In all experiments, we noticed the formation of the corresponding alkane, resulting most likely from the reaction of the carbon–carbon double bond with molecular hydrogen catalyzed by metallic palladium Pd(0). This assumption was based on our previous work on the reaction of the Et_3SiH–$PdCl_2$ system with 1-alkenes.[36] It was suggested that the reaction of Et_3SiH with $PdCl_2$ leads to the formation of Et_3SiCl, metallic palladium and molecular hydrogen [equation (2)]. In this hypothesis, it is possible to completely reduce C=C double bonds of simple alkenes to saturated



Scheme 4.

Table 2. Isomerization of 1-alkenes in the presence of Et_3SiH–Pd on activated charcoal: 1 equiv./10 mol%

Entry		1-Alkene[a]	2-Alkene[b]	3-Alkene[b]	*n*-Alkane[a]	Yield (%)
1-Octene	A	4	46	21	29	67
	B	11	56	23	10	79
	C	7	59	24	10	83
1-Decene	A	16	48	21	15	69
	B	40	36	20	4	56
	C	25	46	24	5	70
1-Dodecene	A	52	19	14	15	33
	B	54	30	12	4	42
	C	27	43	25	5	68
1-Tetradecene	A	57	16	12	14	28
	B	35	36	21	6	57
	C	34	38	22	6	60
1-Hexadecene	A	70	19	7	4	26
	B	52	28	16	4	44
	C	50	29	16	5	45
1-Octadecene	A	23	56	11	10	67
	B	27	44	20	9	64
	C	24	48	19	9	67

[a] Determined by GC/MS analysis.
[b] Determined by GC/MS analysis for *cis* and *trans* mixtures.
A: after 17 h at room temperature; B: after 6 h at 50 °C; C: after 10 h at 50 °C.

Table 3. Isomerization of 1-alkenes in the presence of Et_3SiH–$Pd(OAc)_2$: 1 equiv./10 mol%

Entry		1-Alkene[a]	2-Alkene[b]	3-Alkene[b]	*n*-Alkane[a]	Yield (%)
1-Octene	A	16	48	29	7	77
	B	7	60	25	7	85
1-Decene	A	27	34	18	21	52
	B	10	57	27	6	84
1-Dodecene	A	15	40	22	23	62
	B	24	45	25	7	70
1-Tetradecene	A	38	34	21	7	55
	B	24	44	25	7	69
1-Hexadecene	A	41	28	19	12	47
	B	19	50	24	7	74
1-Octadecene	A	14	42	25	19	67
	B	18	46	28	8	74

[a] Determined by GC/MS analysis.
[b] Determined by GC/MS analysis for *cis* and *trans* mixtures.
A: after 6 h at room temperature; B: after 6 h at 50 °C.

alkanes by operating in the presence of an excess of triethylsilane. In the case of the Pd–C–Et_3SiH system, the palladium is in its reduced form and the generation of molecular hydrogen is only possible by the formation of $(Et_3Si)_2$ (Scheme 3). It is important to note that the yield of the corresponding alkane decreased when the temperature was increased from room temperature to 50 °C. This result might account for hydrogen desorption from the metal catalyst at 50 °C.

In the next step, we have used $Pd(OAc)_2$ as a catalyst instead of Pd–C. Initially, the isomerization reaction of 1-alkenes was conducted at room temperature for 3 days. For example, the reaction of 1 equiv. of 1-tetradecene with Et_3SiH–$Pd(OAc)_2$ (1 equiv./10 mol%) for 3 days at room temperature led to the formation of 1-tetradecene–2-tetradecene–3-tetradecene–tetradecane in 27 : 40 : 25 : 7% ratio. However, comparable results were obtained only after 6 h reaction at room temperature. This result indicates that prolonged reaction times do not have a significant influence on the reaction distribution and yield. Good conversions and yields were obtained when 1 equiv. of 1-alkene was reacted with 1 equiv. of Et_3SiH in the presence of 10 mol% $Pd(OAc)_2$ for 6 h at room temperature. The results are summarized in the Table 3. As previously, the effect of the temperature on the conversion yield was examined. High conversions and yields (69–85%) were obtained when the temperature of the reaction was increased to 50 °C. For example, the reaction of 1-decene and 1-hexadecene at room temperature gave a mixture of different products in 52 and 47% yield, respectively. The same reaction conducted at 50 °C gave a ratio of different isomers (10 : 57 : 27 : 6 and 19 : 50 : 24 : 7%) at 84 and 74% yield, respectively.

A comparable trend to Pd on charcoal catalyst was observed for the reaction distribution at 50 °C. Indeed, the yield of the resulting alkane decreased when the temperature was increased from room temperature to 50 °C.

When Pd–C was used as a catalyst, a low conversion yield and a high concentration of the reduced material were observed. The system $Pd(OAc)_2$–Et_3SiH is more effective than the Pd on activated charcoal–Et_3SiH system and the reaction times are shorter. The acceleration of the reaction rate is due most likely to the formation of a catalytic active Pd(0) by the reduction of $Pd(OAc)_2$ with triethylsilane. For both catalysts, no hydrosilylation of the alkenes occurred. These results are comparable to the previous ones obtained with Et_3SiH–$PdCl_2$ system. Even though there are similarities with the obtained results, it is hard to draw a general conclusion about the trends of the palladium-catalyzed C=C double bond isomerization.

In summary, this work demonstrates the high efficiency for reduction of alkenes to the corresponding alkanes using $Pd(OAc)_2$ or Pd–C, triethylsilane and ethanol as solvent, at room temperature. We have shown that the Et_3SiH–$Pd(OAc)_2$ system can also serve as a very efficient reagent for the carbon–carbon double bond isomerization. The efficiency and the experimental simplicity of the present method are valuable in comparison with the methods previously employed for the reduction and isomerization of 1-alkenes.[13,18,31] No hydrosilylation reaction takes place with this system. The ready availability of the catalyst, the high yields and the simplicity of the procedure render this methodology advantageous. The absence of solvent in isomerization reactions is beneficial from an environmental point of view. Further investigations using the same catalyst for other chemical transformations are currently in progress.

EXPERIMENTAL SECTION

All manipulations were carried under an argon atmosphere. 1-Octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene were purchased from Aldrich and distilled. Ethanol and triethylsilane were obtained from Aldrich and used without further purification. The reported yields are based on GC/MS analysis using a Fison GC 8000 series Trio 1000 gas chromatograph equipped with a column capillary CP Sil.5 CB, 60 m × 0.25 mm i.d.

General procedure for reduction of 1-olefins

To a solution of 1-alkene (0.2 g, 1 equiv.) and triethylsilane (2 equiv.) in 10 ml ethanol were added a catalytic amount of palladium(II) acetate or palladium on activated charcoal (10 mol%) under an argon atmosphere. The resulting mixture was stirred for 1 day at room temperature prior to GC/MS analysis.

General procedure for isomerization of 1-olefins

To a solution of 1-alkene (0.2 g, 1 equiv.) and triethylsilane (1 equiv.) was added a catalytic amount (10 mol%) of palladium on activated charcoal or palladium(II) acetate at room temperature under an argon atmosphere. The resulting mixture was stirred for indicated time at room temperature (or at 50 °C) and then 10 ml of hexane were added to the mixture. The residue was filtered over silica gel (to remove the palladium salts) and the filtrate was evaporated. The crude product was analyzed by GC/MS.

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