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Short communication

A novel and efficient method for double bond isomerization

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Abstract

Isomerization of α-alkenes is carried out in the presence of a catalytic amount of palladium (II) chloride and triethylsilane at room temperature. This novel and efficient method affords high yields in the absence of solvent for double bond isomerization of alkenes.

Keywords: Isomerization; α-Alkenes; Palladium (II) chloride; Triethylsilane

1. Introduction

Double bond shift is one of the major industrial processes in the context of petrochemical oil-refining steps and follows the thermodynamic driving forces. Selective olefin isomerization under mild conditions is therefore a goal that merits increased attention of the organometallic chemists. Diverse processes for olefin isomerization continue to be topics of widespread interest [1,2]. π-Coordination of transition metals such as rhodium and nickel facilitates the attainment of the thermodynamic equilibrium under mild conditions.

In some cases, however, the double bond isomerization is an undesirable reaction. When the transition metal complex induces catalytically both a reaction at the double bond and its isomerization, the kinetics and the product distribution are affected and thus the selectivity of the reaction.

Silicon hydrides have met successful applications in substitution, reduction and addition processes [3–5]. Most of these reactions are catalyzed by transition metal complexes. The combination of organosilicon reagents and palladium (Pd) complexes provides additional examples of the versatility of organosilanes as useful precursors in organic chemistry [6]. Synthetic applications of silicon hydrides with palladium dichloride have already been reported for the reduction of Schiff-bases [7] and the preparation of halosilanes [8]. More recently, palladium dichloride ($PdCl_2$) was used as a catalyst for the conversion of organic halides to the corresponding alkanes by triethylsilane [9]. Moreover, the versatile behavior of the $PdCl_2/R_3SiH$ system was demonstrated in a wide variety of transformations: conversion of alcohols to the corresponding silyl ethers, halides and alkanes [10].

This letter investigates the reactivity of the system $Et_3SiH/PdCl_2$ in the presence of α-olefins. We will report the use of $Et_3SiH/PdCl_2$ system as an extremely efficient method for the isomerization of α-olefins in the absence of solvent under mild conditions.

2. Results and discussion

At earlier stage of our work, we have investigated the efficiency of $Ph_3SiH/PdCl_2$ system for the carbon–carbon double bond isomerization. In a typical experiment, addition of palladium dichloride (20 mol.%) to a stirred mixture of 1-alkene (0.2 g, one equivalent) and triphenylsilane (0.5 equivalent) in 10 ml of dry hexane at room temperature under an argon atmosphere gave only 10% conversion of 1-alkene to 2- and 3-alkenes. This result is somehow deceptive because of the low conversion yield. In the next step, we have used triethylsilane

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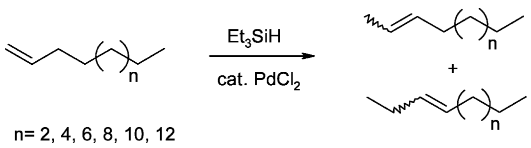


Scheme 1.

instead of triphenylsilane without any solvent. As previously, to a stirred mixture of 1-alkene and triethylsilane was added a catalytic amount of palladium dichloride at room temperature. GC/MS analysis shows the formation of isomers 2-alkene and 3-alkene (*cis–trans* mixtures) accompanied with the corresponding alkane. The isomerization of α-olefins is outlined in Scheme 1.

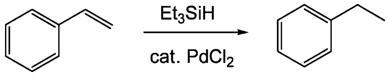
We have tried different experimental conditions in order to optimize the conversion of 1-alkene to its isomers 2- and 3-alkenes. In the first set of experiments, we have carried out the reaction of one equivalent of 1-alkene in the presence of $Et_3SiH/PdCl_2$ (0.2 equivalent/10%). We have found that the conversion and the reaction yields are still low. The results are summarized in Table 1.

For example, the reaction of one equivalent of 1-dodecene with $Et_3SiH/PdCl_2$ (0.2 equivalent/10%) for 17 h at room temperature led to a low conversion. The resulting ratio of 1-dodecene/2-dodecene/3-dodecene/dodecane was 48/31/18/3%. Comparable results were obtained with 1-tetradecene, 1-hexadecene and 1-octadiene. Increasing the amount of Et_3SiH in the reaction mixture ($Et_3SiH/PdCl_2 = 0.5$ equivalent/10%) increases the conversion yield. Reaction of 1-tetradecene with $Et_3SiH/PdCl_2$ (0.5 equivalent/10%) for 7 h at room temperature gave a ratio of the different isomers (25/52/16/7%) in 68%. The reaction time and palladium chloride concentration have also an influence on the product distribution. The reaction of one equivalent of 1-dodecene with $Et_3SiH/PdCl_2$ (one equivalent/20%) for 3 days at room temperature yielded 5/79/10/6% of the different isomers.

Good conversions and yields were obtained when one equivalent of 1-alkene was reacted with one equivalent of Et_3SiH in the presence of 10% $PdCl_2$ for 6 h at room temperature. The results are summarized in the Table 2.

In the next step, we have tested the efficiency of the C=C double bond isomerization over the hydrosilylation reaction. In this purpose, we have studied the reaction of styrene with $Et_3SiH/PdCl_2$ under the same conditions. After 17 h reaction at room temperature, GC/MS and ^{1}H-NMR analysis showed only the formation of ethylbenzene (51%) resulting from hydrogen addition to the C=C double bond (Scheme 2). There was no detectable products arising from addition of Et_3SiH across the C=C double bond or dehydrogenative silylation as previously observed for cationic Pd (II) complexes [11].

The efficiency and the experimental simplicity of the present method are very appreciated in comparison with the methods previously employed for the isomerization



Scheme 2.

Table 1
Isomerization of 1-alkenes in the presence of $Et_3SiH/PdCl_2$: 0.2 equivalent/10% after 17 h at room temperature

Entry	1-Alkene [a] %	2-Alkene [b] %	3-Alkene [b] %	*n*-Alkane [a] %	Yield %
1-Dodecene	48	31	18	3	49
1-Tetradecene	50	28	18	4	46
1-Hexadecene	61	27	10	2	37
1-Octadecene	62	24	11	3	35

[a] Determined by GC/Ms analysis.
[b] Determined by GC/Ms analysis for *cis* and *trans* mixtures.

Table 2
Isomerization of neat 1-alkenes using $Et_3SiH/PdCl_2$: 1/10% after 6 h at room temperature

Entry	1-Alkene [a] %	2-Alkene [b] %	3-Alkene [b] %	*n*-Alkane[a] %	Yield %
1-Octene	8	65	12	15	77
1-Decene	16	50	26	8	76
1-Dodecene	13	56	27	4	83
1-Tetradecene	21	50	18	11	68
1-Hexadecene	3	71	3	23	74
1-Octadecene	10	66	7	17	73

[a] Determined by GC/Ms analysis.
[b] Determined by GC/Ms analysis for *cis* and *trans* mixtures.

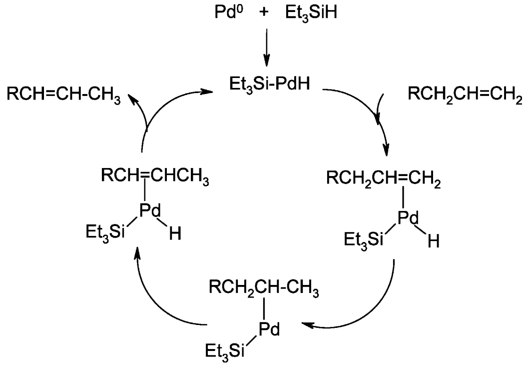
$$2\ Et_3SiH \quad + \quad PdCl_2 \longrightarrow 2\ Et_3SiCl \quad + \quad Pd^0 \quad + H_2$$

Scheme 3.

of 1-alkenes. For example, the isomerization process that involves contacting olefins with a titanium catalyst on alumina in the presence of water [2f] takes place at 300–570 °C, whereas with $Et_3SiH/PdCl_2$ the migration occurs at room temperature in the absence of solvents. Birdwhistell et al. have reported the isomerization of 1-heptene in the presence of $Ni[P(OEt)_3]_4$. This reaction is initiated by adding H_2SO_4 to an ether solution of 1-heptene and $Ni[P(OEt)_3]_4$ at 0 °C [12]. $Ni[P(OEt)_3]_4$, however, is not very stable. It decomposes upon exposure to air and requires special care during its transfer and manipulation.

In earlier studies by some among us on the reduction of alkyl bromides and iodides with $Et_3SiH/PdCl_2$, we have observed the formation of small amounts of Et_3SiCl and molecular hydrogen along with triethylsilyl bromide and triethylsilyl iodide, respectively. This result allowed us to suggest the formation of metallic Pd according to the reaction pathway below (Scheme 3) [8b,10].

We believe that the reaction mechanism is a stepwise process. In the first step, metallic Pd was generated by the reduction of palladium dichloride with Et_3SiH (Scheme 3). This Pd (0) serves as active entity in the catalyzed isomerization reaction and accounts for the formation of the corresponding alkane. The second step consists on the formation of a palladium complex by an oxidative addition of Et_3SiH to the metallic palladium followed by a reductive elimination with a 1,2-hydride shift to produce the first isomerization [8b,13]. The second migration of the carbon–carbon double bond takes place in a similar manner (Scheme 4). The hydrogenation product results from addition of molecular hydrogen (generated from the reaction of Et_3SiH with $PdCl_2$) to the double bond, catalyzed by Pd (0) [14]. Surprisingly, there was no formation of other products resulting from additional isomerization of the double bond or from hydrosilylation reaction even for longer reaction times.



Scheme 4.

In conclusion, we have shown that the $Et_3SiH/PdCl_2$ system is very efficient for the carbon–carbon double isomerization. The reaction is simple and easy to carry out. The migration of the carbon–carbon double bond is self-limited and no hydrosilylation reaction takes place during the isomerization process. It should be noted that the absence of solvent in these reactions is beneficial from an environmental point of view. Further investigations using the same catalyst for other chemical transformations are currently in progress.

3. Experimental

All manipulations were carried under an argon atmosphere. Hexane was distilled over sodium and stored under argon. The reported yields are based on GC/Ms analysis using a FISON GC 8000 series TRIO 1000 gas chromatography equipped with a column capillary CP Sil.5 CB, 60 M × 0.25 mm i.d.

3.1. *General procedure for isomerization of the α-olefins*

To a solution of 1-alkene (0.2 g, one equivalent) and triethylsilane (one equivalent) was added a catalytic amount of palladium (II) chloride (10 mol.%) at room temperature under an argon atmosphere. The resulting mixture was stirred for indicated time at room temperature (see Table 1) and then 10 ml of hexane was added to the solution. 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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