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The versatile behavior of the $PdCl_2/Et_3SiH$ system. Conversion of alcohols to the corresponding halides and alkanes

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Abstract

The versatility of the palladium(II) chloride/triethylsilane system has been tested in the transformation of alcohols. The conversion to the corresponding halides and alkanes has been achieved in good yields and in the absence of solvent for a variety of substrates. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Organosilicon reagents play a prominent role in organic synthesis and are widely applied in functional group transformation. Recently, among group-14 metal hydrides, silicon hydrides have found successful application in reduction, substitution and addition processes in both ionic [1,2] and radical [3] fashion due to their selectivity, efficiency and low toxicity. The synthetic applicability of organosilicon reagents has also been augmented through the use of Pd(II) and Pd(0) complexes [4]. However, the combination of silicon hydrides with palladium dichloride has been reported in only few cases, i.e. for the deprotection of amino acids or peptides [5], nucleophilic substitutions at silicon [6,7], the reduction of Schiff bases [8], and the preparation of halosilanes [9,10].

Following our study carried out on the $PdCl_2$-catalyzed reduction of organic halides by triethylsilane [11], we investigated the reactivity of this system in the presence of alcoholic functions. Herein we report our preliminary results which account for the versatility of the $PdCl_2/Et_3SiH$ couple in the transformation of alcohols to the corresponding halides and alkanes in the absence of solvent.

2. Results and discussion

When $PdCl_2$ (2 mol%) was added to an appropriate mixture of halogenating agent (i.e. CH_3I, CH_2Br_2 or CCl_3CCl_3) and Et_3SiH, an exothermic reaction took place, after which the alcohol was immediately added. Products analyses were carried out using GC with authentic samples as calibrants. Yields were quantified by using an internal standard. The results are summarized in Table 1 [12]. These reactions were accomplished in high yield and in different reaction times, depending on the nature of the starting alcohol but do not suffer from other competitive processes (i.e. elimination). Iodination, bromination and chlorination are very efficient for benzyl, allyl and tertiary alcohols, mild heating seldom being required. Inspection of the data in Table 1 indicates also the formation of primary and sec-

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Table 1
$Et_3SiH/PdCl_2$ mediated conversion of alcohols to halides[a]

ROH[b]	Halogenating agent[b]	Time (h)/T, (°C)	RX yield[c] (%)
$PhCH_2OH$	CH_3I	0.3/25	98
	CH_2Br_2	1/25	98
	CCl_3CCl_3	5/60	94[d]
$PhCH{=}CHCH_2OH$	CH_3I	1/25	83[d]
	CH_2Br_2	3/25	91
	CCl_3CCl_3	24/60	86
$(CH_3)_3COH$	CH_3I	0.6/25	98
	CH_2Br_2	1.5/25	98
	CCl_3CCl_3	28/60	80
c-$C_6H_{11}OH$	CH_3I	24/25	98
	CH_2Br_2	23/60	89[d]
	CCl_3CCl_3	48/60	80
1-Decanol	CH_3I	24/25	90
	CH_2Br_2	23/60	81
	CCl_3CCl_3	72/60	13
1,4-Butanediol	CH_3I	2/60	96[d]
	CH_2Br_2	23/60	90[d]
	CCl_3CCl_3	24/60	80[d,e]

[a] $PdCl_2$ (2 mol%).

[b] ROH:(hal.agent):Et_3SiH = 1:1:1.4.

[c] Determined by GC analysis on the basis of product formation in the crude reaction mixture using an internal standard.

[d] 2.8 equiv. of Et_3SiH.

[e] Products refer to a 1:2:5 ratio of 1-triethylsilyloxy-4-chlorobutane:4-chloro-1-butanol:tetrahydrofurane.

ondary iodides and bromides in good yields with the exception of 1-decanol and cyclohexanol, which gave poor yields of the corresponding chlorides and 1,4-butanediol which could be chlorinated only at one position, the other alcoholic function being mainly transformed into its corresponding silylether. Additional experiments showed that the reaction proceeds with inversion of configuration. For example, optically pure (+)-2-octanol was converted to (−)-2-octyl iodide with an optical purity of 87.3% [13].

A mechanistic picture of these reactions can be deduced by following the reaction course. The identification by GC of small amounts of Et_3SiCl in the reaction with CH_3I and CH_2Br_2 as well as the formation of metallic Pd and the H_2 evolution suggest the following initial step:

$$2Et_3SiH + PdCl_2 \rightarrow 2Et_3SiCl + Pd + H_2 \qquad (1)$$

GC analysis of the mixtures prior to the alcohol addition revealed the in situ formation of the triethylsilyl halide in quantitative yield. The propagation steps for these reactions (Eq. (2)) may involve oxidative addition of the halogenating agent (RX) to Pd followed by reduction of the palladium complex by triethylsilane in analogy with the initiation step[3].

Table 2
$Et_3SiH/PdCl_2$ mediated conversion of alcohols to alkanes

ROH	Method[a]	Time (h)/T (°C)	RH yield[b], (%)
$PhCH_2OH$	A	3/25	98
	B	16/25	98
2-Octanol	A	4/25	98
	B	1/25	98
1-Decanol	A	24/25	90
	B	1/60	80

[a] CH_3I and CH_2Br_2 were used in methods A and B, respectively.

[b] Determined by GC analysis on the basis of product formation in the crude reaction mixture using an internal standard.

$$RX + Pd \rightarrow RPdX \xrightarrow{Et_3SiH} Et_3SiX + Pd + RH \qquad (2)$$

Upon alcohol addition, silyl ethers are initially formed prior to the appearance of the halides[4]. Trialkylsilyl bromides and iodides are known to effect the transformation of alcohols to bromides and iodides [14,15], whereas trimethylsilyl chloride needs some activation [16–18]. On the other hand, trialkylsilyl iodides are efficient for the conversion of silyl ethers to iodides whereas the halogenating ability of bromo trimethylsilane is quite poor [15]. Therefore, the presence of metallic Pd in the reaction mixture may also play a role in the second part of this process.

The transformation of alcohol to the corresponding alkane was also achieved. Following the above protocol, as soon as the alcohol was transformed into its halide (followed by GC), another portion of Et_3SiH was added. This methodology provided the transformation of alcohols to alkanes in an one-pot reaction with very good yields. The results of the reduction process are given in Table 2 [12]. It is quite clear that the reduction of intermediate halides took place with Et_3SiH mediated by metallic Pd in a fashion similar to that illustrated in Eq. (2).

These preliminary results account for the efficiency and flexibility of the palladium catalyzed transformation of alcohols in the presence of organosilicon hydrides. It should also be noted that the absence of solvent in these reactions is beneficial from an environmental point of view [19].

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[3] An alternative mechanism [10], in which the silane first adds oxidatively to the Pd followed by exchange between the silyl and alkyl groups, cannot be ruled out at present.

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[12] Typical Procedure: To a stirred mixture of Et_3SiH (0.22 mL; 1.4 mmol) and $PdCl_2$ (12 mg; 0.028 mmol) kept under argon in a Wheaton® reactor equipped with a Mininert® syringe valve at room temperature, CH_2Br_2 (0.07 ml; 1 mmol) was added. An exothermic reaction occurred, after which 1-decanol (0.19 ml; 1 mmol) was added and the reaction mixture heated at 60°C for 23 h. GC analysis showed the formation of 1-bromo decane in 81% yield. Another portion of Et_3SiH (0.22 ml; 1.4 mmol) was added by syringe and heating at 60°C was continued for another hour to afford 1-decane in 80% yield.
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