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A simple and efficient hydrogenation of benzyl alcohols to methylene compounds using triethylsilane and a palladium catalyst

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ABSTRACT

Hydrogenolysis of benzyl alcohols using triethylsilane (Et_3SiH) and a catalytic amount of palladium(II) chloride ($PdCl_2$) is described. The reaction takes place under mild conditions affording high yields of the corresponding methylene compounds in short reaction times.

Heterogeneous and homogeneous catalytic hydrogenation reactions have found widespread applications in the reduction of a large variety of functional groups.[1–3]

Benzyl alcohols are often used in organic synthesis, either as starting materials or as protecting groups.[4–7] Hydrogenolysis of benzyl alcohols has been described in several reports. For example, benzyl alcohols are readily converted into tetrazolyl and benzisothiazolyl ethers which can be catalytically hydrogenolyzed into toluenes over palladium-on-charcoal in good yields using hydrogen donors.[8] Hydrogen iodide, generated (and regenerated) in situ by the action of iodine upon hypophosphorus acid, was found to reduce a variety of aryl carbinols to the corresponding diphenylmethanes under mild conditions.[9] The reduction of primary, secondary, and tertiary benzylic alcohols to their corresponding hydrocarbons was performed in a two-phase system [apolar organic solvent and 50% KOH(aq)] at 50 °C, using 5% Pd/C and H_2 at atmospheric pressure. The reaction requires the presence of aromatic halides. In the absence of the halide promoter, the reaction takes place only if a halogen is present on the aromatic ring of the alcohol.[10] The use of trialkylborons with trifluoromethanesulfonic acid was found to be an effective reducing system for the conversion of a variety of tertiary, secondary, and benzylic alcohols into the corresponding alkanes, as well as alkylated alkanes.[11] The Raney Ni–sulfuric acid system was successfully applied for the reduction of several aryl bromides, benzyl alcohols, benzyl ethers, and benzylamines under mild conditions. Although details of the reaction mechanism for this reduction are not clear, reductive cleavage of the substrate is believed to proceed by utilizing both the adsorbed hydrogen on the Raney Ni and the hydrogen generated by the reaction between Raney Ni and sulfuric acid.[12]

Furthermore, organosilicon reagents in the presence of small amounts of a catalyst are used for the reduction of functional groups. The combination of chlorodimethylsilane and a catalytic amount of an indium compound is effective for the deoxygenation of aryl ketones and *sec*-benzylic alcohols to give the corresponding hydrocarbons.[13,14] Finally, ionic reduction of alcohols and ketones with triethylsilane/trifluoroacetic acid (Et_3SiH/CF_3CO_2H) was described by Mayr.[15]

We have investigated the efficiency of the $Et_3SiH/PdCl_2$ system for the hydrogenation of 1-alkenes under mild conditions,[16,17] for the transformation of alcohols into their corresponding silyl ethers and for the cleavage of triethylsilyl ethers to the parent alcohols.[18] Furthermore, the versatility of the $Et_3SiH/PdCl_2$ system was demonstrated for the selective hydrogenation of the carbon–carbon double bond of α,β-unsaturated ketones to afford the corresponding saturated ketones under mild conditions.[19] More recently, this system was used for the reduction of carbonyl groups of aromatic aldehydes and ketones into a methylene group.[20] The results indicated the formation of the corresponding alcohol as an intermedi-

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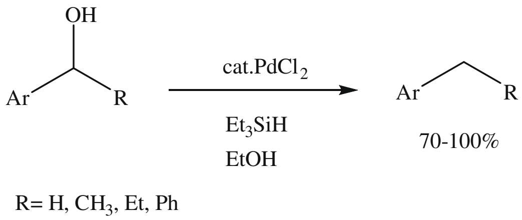
ate during the reduction of aromatic aldehydes. Based on the above observation, the present work was aimed at exploring the efficiency of molecular hydrogen, generated in situ by the reaction of Et_3SiH with EtOH in the presence of a catalytic amount of $PdCl_2$, for the reduction of benzyl alcohols to the corresponding methylene compounds.

Reduction of various benzyl alcohols with Et_3SiH in the presence of palladium dichloride in ethanol occurs at room temperature to yield the corresponding methylene products in high yields (Scheme 1, Table 1).

The hydrogenation reaction requires the use of an inert atmosphere and anhydrous solvent. In a typical experiment, $PdCl_2$ (10 mol %) was added at room temperature to a stirred mixture of alcohol (1 equiv) and Et_3SiH (2 equiv) in dry ethanol (5 ml). An exothermic reaction occurs during the first 5 min and then the temperature decreases to room temperature. The resulting mixture was stirred for the time indicated in Table 1 prior to GC–MS analysis.

The reduction of the benzyl alcohols takes place quantitatively. For example, the reaction of 1 equiv of benzyl alcohol (Table 1, entry 1), 4-methoxybenzyl alcohol (Table 1, entry 2) and 1-phenylethanol (Table 1, entry 7) with $Et_3SiH/PdCl_2$ (2 equiv/10%) in ethanol (5 ml) for 10 min at room temperature led to the formation of toluene, 4-methylanisole and ethylbenzene, respectively, in 100% yields. Likewise, the reaction of 4-hydroxy-3-methoxybenzyl alcohol (Table 1, entry 4), 4-*tert*-butyl-benzyl alcohol (Table 1, entry 6) and 1-phenyl-1-propanol (Table 1, entry 8) gave 2-methoxy-4-methylphenol, 4-*tert*-butyltoluene and propylbenzene in 96%, 90% and 95% yields, respectively. Increasing the reaction time to 30 min led to an increase in the yield to 95% for entry 6.



Scheme 1.

It should be noted that for certain compounds an excess of triethylsilane or longer reaction times were required to drive the reaction to completion. For example, the reaction of 2-biphenyl-4-ylpropan-2-ol (Table 1, entry 9) with Et_3SiH (alcohol/Et_3SiH: 1/2 or 1/4) produced, respectively, 72% and 82% yields of the corresponding product after 30 min. However, high conversion (96%) was obtained when the reaction was conducted in the presence of an excess of triethylsilane (alcohol/Et_3SiH: 1/6). Similarly, the reaction of the secondary alcohol benzhydrol (Table 1, entry 10) with 2 equiv of Et_3SiH in the presence of $PdCl_2$ led to the formation of diphenylmethane in 87% yield, after 30 min at room temperature. The yield was increased to 100% by increasing the reaction time to 1 h under the same conditions. A yield of 100% was obtained when the ratio of benzhydrol/Et_3SiH was increased to 1/3, after 30 min at room temperature. 1-Indanol was converted quantitatively into indane with 2 equiv of Et_3SiH after 10 min at room temperature. We also observed the reduction of conjugated alcohols such as cinnamyl alcohol to propylbenzene using 8 equiv of Et_3SiH in 94% yield after 10 min at room temperature. Finally, we examined the hydrogenolysis of heterocylic alcohol derivatives. A trace amount of 3-methylpyridine was obtained after 1 h at room temperature in ethanol when the reduction of 3-pyridinylmethanol was carried out using 2 equiv of Et_3SiH. Using an excess of triethylsilane (8 equiv) and performing the reaction at reflux gave 3-methylpyridine in high yield (95%) after 4 h. On the other hand, thiophene-2-methanol was readily reduced to 2-methylthiophene in 70% yield using 6 equiv of Et_3SiH in the presence of $PdCl_2$, after 4 h at room temperature.

Next, we investigated the hydrogenolysis of aliphatic alcohols such as 1-heptanol and 1-decanol using the $Et_3SiH/EtOH/PdCl_2$ system. The reduction failed to proceed under these conditions, even in the presence of a large excess of Et_3SiH. Indeed, no reaction oc-

Table 1
Reduction of benzyl alcohols to the corresponding methylene compounds using $Et_3SiH/PdCl_2$ in ethanol

Entry	Substrate	Product	Substrate/Et_3SiH	Time (min)	Yield[a] (%)
1	Benzyl alcohol	Toluene	1/2	10	100
2	4-Methoxybenzyl alcohol	4-Methylanisole	1/2	10	100
3	2-Methoxybenzyl alcohol	2-Methylanisole	1/2	10	98
4	4-Hydroxy-3-methoxybenzyl alcohol	2-Methoxy-4-methylphenol[21]	1/2	10	96
5	2-Hydroxybenzyl alcohol	*o*-Cresol	1/2	30	90
6	4-*tert*-Butyl-benzyl alcohol	4-*tert*-Butyltoluene	1/2	10	90
7	1-Phenylethanol	Ethylbenzene	1/2	10	100
8	1-Phenyl-1-propanol	Propylbenzene	1/2	10	95
9	2-Biphenyl-4-ylpropan-2-ol	4-Isopropylbiphenyl	1/2	30	72
			1/4	30	82
			1/6	30	96
10	Benzhydrol	Diphenylmethane	1/2	30	87
			1/2	60	100
			1/3	30	100
11	1-Indanol	Indane	1/2	10	100
12	Cinnamyl alcohol	Propylbenzene	1/4	10	80
			1/6	10	86
			1/8	10	94
13	3-Pyridinylmethanol	3-Methylpyridine	1/2	60	Trace
			1/6	240	34
			1/6	60	85[b]
			1/8	240	95[b]
14	Thiophene-2-methanol	2-Methylthiophene	1/2	60	24
			1/6	60	54
			1/6	240	70

[a] Determined by GC–MS.
[b] The reaction was conducted at reflux.

Table 2
Reduction of benzyl alcohol with Et_3SiH (1/2) with different palladium catalysts in the absence of a solvent at room temperature

Entry	Catalyst	Time	PhMe/$BnOSiEt_3$/BnOH[a] (%)
1	$PdCl_2$ (10%)	20 min	50/50/0
2	$Pd(OAc)_2$ (10%)	20 min	8/78/14
3	$PdCl_2$ (1 equiv)	5 min	100/0/0
4	$Pd(OAc)_2$ (1 equiv)	15 min	16/27/57
5	$Pd(OAc)_2$[b] (10%)	19 h	84/3/2[c]

[a] Determined by GC–MS.

[b] The reaction was conducted in the presence of 1 equiv of $Cl_3C–CCl_3$ as halogenating agent.

[c] 11% of benzyl chloride was also obtained.

curred after 30 min at room temperature in ethanol in the presence of 6 equiv of Et_3SiH, or when using 10 equiv of Et_3SiH in the presence of $PdCl_2$ at reflux for 4 h, and only the starting material was recovered. However, when the reaction was performed for 22 h at room temperature in the presence of excess Et_3SiH (alcohol/Et_3SiH: 1/10), the corresponding triethylsilyl ethers were obtained in 62% and 56% yields along with 38% and 44% yields of the starting alcohols, respectively.

We also examined the reduction of benzyl alcohol by Et_3SiH in the presence of catalytic amounts of $PdCl_2$ or $Pd(OAc)_2$ in the absence of solvent (ethanol). The reaction of benzyl alcohol with Et_3SiH (1/2) in the presence of 10% $PdCl_2$ gave 50% of toluene and 50% of the corresponding triethylsilyl ether after 20 min at room temperature (Table 2, entry 1). Under the same conditions, $Pd(OAc)_2$ as the catalyst afforded only an 8% yield of toluene, 78% of the corresponding triethylsilyl ether, and 14% of the starting alcohol (Table 2, entry 2). On the other hand, the use of 1 equiv of $PdCl_2$ in the absence of ethanol yielded quantitatively, toluene, after only 5 min (Table 2, entry 3). In contrast, only partial reduction of benzyl alcohol was observed when the reaction was performed in the presence of 1 equiv of $Pd(OAc)_2$ (Table 2, entry 4). These results clearly indicate the influence of the chloride ions (or Et_3SiCl) on the reaction mechanism. Thus we investigated the reduction of benzyl alcohol with $Pd(OAc)_2$ as the catalyst in the presence of a halogenating agent such as $Cl_3C–CCl_3$. The reaction of benzyl alcohol with Et_3SiH (1/2) in the presence of 10% $Pd(OAc)_2$ as catalyst and 1 equiv of $Cl_3C–CCl_3$ yielded 84% of toluene, 3% of benzyloxytriethylsilane, 11% of benzyl chloride, and 2% of the starting alcohol under solvent-free conditions after 19 h at room temperature (Table 2, entry 5). We also performed the reduction of benzyl chloride using $PdCl_2$ as the catalyst in the presence of 2 equiv of Et_3SiH and the reduction to toluene was complete after 5 min at room temperature.

The results suggest that chloride ions might play a role in the reduction mechanism. This is corroborated by previous reported work on the reduction of alcohols into their corresponding halides and alkanes using the $Et_3SiH/PdCl_2$ system in the presence of a halogenating agent.[22] Furthermore, addition of a halogenating agent such as $Cl_3C–CCl_3$ to the reaction mixture led to an increase in the yield for the reduction of benzyl alcohol by Et_3SiH in the presence of $Pd(OAc)_2$. However, in the present work, the reduction of benzylic alcohols does not require the presence of a halogenating agent. The only potential source of halogen is Et_3SiCl, resulting from reduction of $PdCl_2$ by Et_3SiH, as previously suggested.[23] Thus it is hard to draw a final conclusion regarding the exact reaction mechanism at this stage.

In conclusion, we have developed a simple and highly efficient method for the hydrogenolysis of benzyl alcohols to the corresponding methylene compounds using Et_3SiH in ethanol in the presence of a catalytic amount of $PdCl_2$. The reaction is easy to carry out affording high yields of the corresponding products.

General procedure for the reduction of alcohols: To a solution of alcohol (1 mmol, 1 equiv) and triethylsilane (amount indicated in Table 1) in ethanol (5 ml) was added a catalytic amount of palladium(II) chloride (10 mol %) under an argon atmosphere. The resulting mixture was stirred for the time indicated in Table 1 prior to GC–MS analysis. The pure products in entries 1 and 7 were isolated by distillation, and those for entries 2–6 and 8–10 were isolated by column chromatography using hexane/ethyl acetate (9/1) as eluent. The products[24] were characterized by ^1H NMR spectroscopy and mass spectrometry.

Entry 9, Table 1, ^1H NMR ($CDCl_3$, 80 MHz): $\delta = 1.42$ (d, $J = 5.3$ Hz, 6H, CH_3), 3.06 (m, 1H, CH), 7.34–7.77 (m, 9H, CH arom.). MS (70 eV), m/z (%): 196 (62) (M^+), 181 (100).

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