

Efficient Palladium-Catalyzed C–O Hydrogenolysis of Benzylic Alcohols and Aromatic Ketones with Polymethylhydrosiloxane

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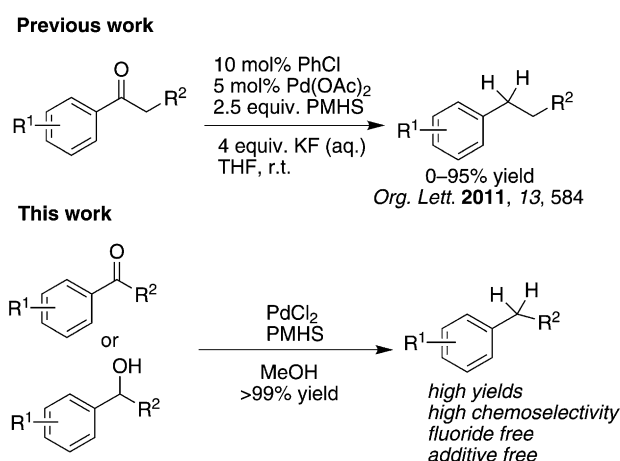
Abstract: A simple method has been developed for the reductive deoxygenation of aromatic ketones and benzylic alcohols in the presence of polymethylhydrosiloxane (PMHS). The reductive deoxygenation of aromatic ketones and benzylic alcohols, including secondary alcohols, to the corresponding methylene hydrocarbons has been achieved in good to excellent yields using palladium chloride (PdCl₂) as catalyst and PMHS as hydride source. Such deoxygenations were successfully with aryl alkyl ketones and diaryl ketones, as exemplified by the reductive deoxygenation of acetophenone and benzophenone, respectively. The corresponding benzylic alcohols and secondary alcohol analogues could also be converted into their respective methylene hydrocarbons by the PdCl₂/PMHS system.

Keywords: deoxygenation; hydrogenolysis; palladium; reduction; polymethylhydrosiloxane (PMHS); silanes

Polymethylhydrosiloxane (PMHS) is an important reducing agent for eco-friendly reductive processes on organic functional groups because it is a safe, easy-to-handle, cheap and environmentally benign reagent. It is a by-product of the organosilicon industry and an inexpensive hydrosilane that can be employed as the stoichiometric reducing agent in organic synthesis.^[1] In the context of PMHS, the development of cleaner, more chemoselective, and safer synthetic methods and technologies for the reduction of functional groups to meet ever stricter environmental regulations remains an active area in organic chemistry.^[2] In

the past decades, PMHS has been used in the hydrosilylation or reduction of carbonyl compounds,^[3] imines,^[4] olefins,^[5] or alkynes^[6] that require activation with a transition metal complex, fluoride ion or a Lewis acid.^[3–7] We have also previously reported that the combinational use of polymethylhydrosiloxane and malononitrile as reductive system could allow for the bismuth-catalyzed regioselective formation of substituted ketones from enones under mild conditions.^[8]

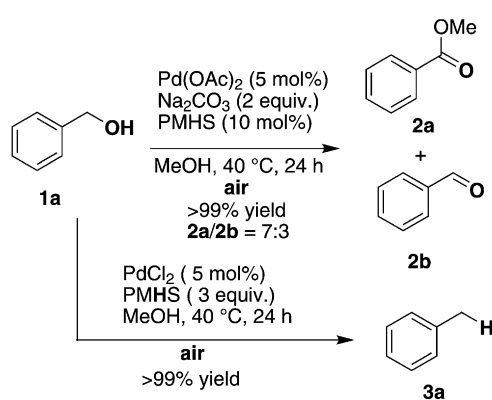
Although the palladium-catalyzed selective 1,4-reduction of α,β -unsaturated ketones in the presence of PMHS is known,^[9] the 1,2-reduction of ketones is not an easy task for palladium catalysis. Thus we are interested in the development of a highly efficient palladium catalyst encapsulated in a polysiloxane gel to reduce ketones to alcohols or alkanes completely in the presence of PMHS. In this context, Maleczka et al.^[10] has reported very recently an important and effective catalytic system with Pd(OAc)₂ (5 mol%) and PMHS (2.5 equiv.) in conjunction with aqueous KF (4 equiv.) and a catalytic amount of aromatic chloride (10 mol%) that promoted the highly chemoselective deoxygenation of aromatic ketones. The ability to achieve such a reductive deoxygenation is highly attractive, since it allows the rapid, efficient, and selective construction of alkanes in excellent yields. Although the preparative advantages of fluoride activation in terms of reaction rate, generality, and stereoselectivity in the synthetic applications of hydrosilane have been known for many years, the cost and corrosiveness of fluoride sources as well as their incompatibility with common protective groups limit the widespread application of this method. In view of the power of palladium catalysis and the importance of the deoxygenation reaction of aromatic ketones,^[11] we



Scheme 1. Comparison of conventional palladium-based deoxygenation approaches with the PdCl₂/PMHS/MeOH system used in this work

sought to develop a new strategy to achieve the C–O hydrogenolysis of benzylic alcohols and aromatic ketones through fluoride-free palladium catalysis (Scheme 1). With the success of the reductive deoxygenation described above, we could investigate the feasibility and potential of the preparation of various aromatic alkanes *via* palladium-catalyzed reductive deoxygenation.

In our initial investigation of the palladium-catalyzed oxidative esterification of benzylic alcohol in the presence of PMHS,^[12] we noted a significant difference in the reaction results in accord with the reaction conditions. When PMHS was used as an additive in the Pd(OAc)₂-catalyzed transformation of benzylic alcohol (**1a**), the aerobic oxidation reaction occurred smoothly to afford aldehyde and ester. However, treatment of benzylic alcohol with a large amount of PMHS (3 equiv.) in the presence of PdCl₂ afforded toluene by deoxygenation of benzylic alcohol (Scheme 2). Subsequently, we examined a variety of

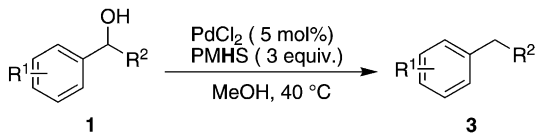


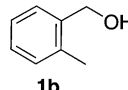

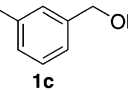

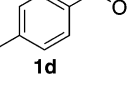

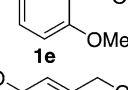

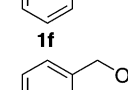

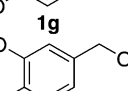

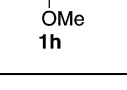

Scheme 2. Transformation of benzyl alcohol catalyzed by palladium in the presence of PMHS.

solvents, of which methanol proved to be the most effective. It was thus clear that the methanol was influencing the reactivity of the palladium-catalyzed deoxygenation of benzylic alcohol. Interestingly, employing 1 mol% of PdCl₂ also led to a reductive deoxygenation in high yield. The observation that 5 mol% of PdCl₂ resulted in complete conversion and excellent yield indicates that the reaction conditions could be suitable for a broad substrate scope.

Under our optimized conditions with 5 mol% of PdCl₂ and 3 equiv. of PMHS, the generality of the reductive deoxygenation reaction was investigated using a number of substituted benzylic alcohols. As shown in Table 1, the reduction reaction of various aromatic alcohols using the same conditions as in the case of benzylic alcohol (**1a**) affords the desired alkanes in excellent yields. For example, the reduction of *o*-tolylmethanol (**1b**), *m*-tolylmethanol (**1c**), or *p*-tolylmethanol (**1d**), gives *o*-xylene (**3b**), *m*-xylene (**3c**), or *p*-xylene (**3d**) in excellent yields, respectively (entries 1–3). The more electron-rich substrates (**1e–1h**) afford the desired products in almost quantitative yields (entries 4–7). As summarized in Table 1, benzylic alcohols substituted at the phenyl ring with MeO, Me, phenyl, hydroxy moieties were all converted into the corresponding alkanes completely. Unfortunately, nitro and halide substituents at the phenyl ring show limited selectivity and led to mixtures under the same reaction conditions because the nitro (NO₂) or halide (Cl) group could be reduced partially to amine (NH₂) or hydrogen (H), respectively (Scheme 3). It is noteworthy that for 4-(hydroxymethyl)phenol (**1i**), *p*-cresol was also isolated in 99% yield (entry 8). We have also investigated the reductive deoxygenation of secondary alcohols, such as 1-phenylethanol and analogues. The results indicated that secondary aryl alcohols could also be successfully transformed into the corresponding products in good to excellent yields (entries 9–19). Generally, aromatic alcohols bearing electron-rich substituents proceeded more efficiently than those of bearing electron-donating substituents. Although some functional groups, such as nitro and halide moieties, exhibited remarkable and negative electronic effects, we were pleased to find that the present palladium-catalyzed reductive deoxygenation proved to be a highly efficient procedure of the preparation of alkanes from aromatic alcohols.

As can be seen from Table 1, the scope of this Pd-catalyzed reductive deoxygenation of benzylic alcohols with PMHS appears to be very broad, and the reaction is satisfactory even with versatile secondary alcohols. Since the ability of PMHS to reduce ketones to alcohols has been recognized in the past,^[13] we hypothesized this reductive system would be expected to achieve the reductive deoxygenation of aromatic ketones. Then the palladium-catalyzed reductive deoxygenation of aromatic ketones was also tested with

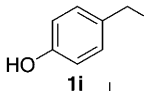
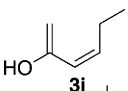








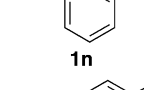











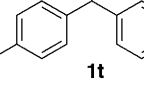
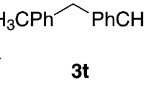
Table 1. Reductive deoxygenation of alcohols by palladium in the presence of PMHS.^[a]


Entry	Alcohol	Product	Time [h]	Yield [%]
1			18	99
2			18	99
3			18	99
4			18	99
5			18	99
6			18	99
7			18	94

PdCl_2 as catalyst and PMHS as reducing agent. As shown in Scheme 4, the reaction conditions were found to be very effective in the reaction of aromatic ketones, and the corresponding alkanes were obtained in good to excellent yields. Notably, the selectivities of all these substrates shown in Scheme 4 were excellent, as no alcohol intermediate was detected. The experiments showed that the reactivities of ketones were the same as those of the corresponding alcohols. Therefore, the excellent chemoselectivity and conversion of present process make it an attractive and practical alternative to the use of aryl chlorides as additives and large amounts of KF as activator of PMHS.

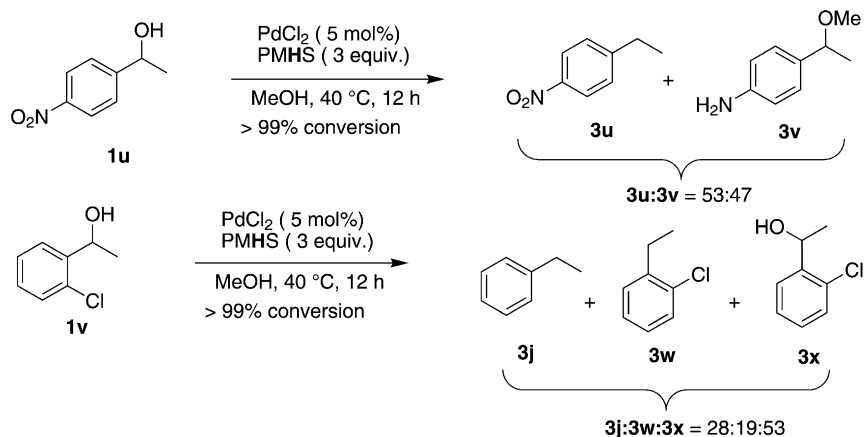
Similarly to alcohol substrates, the reductive deoxygenation of related aromatic ketones containing the nitro or halide substituent resulted in low selectivity under the same reaction conditions. In addition, it is found that the reactivity of unconjugated aromatic ketones with an isolated carbonyl was not good, for example, the reduction of 2-indanone (**4n**, Scheme 5) led to low yield of alkane and poor chemoselectivity. However, these unexpected products provided some

Table 1. (Continued)

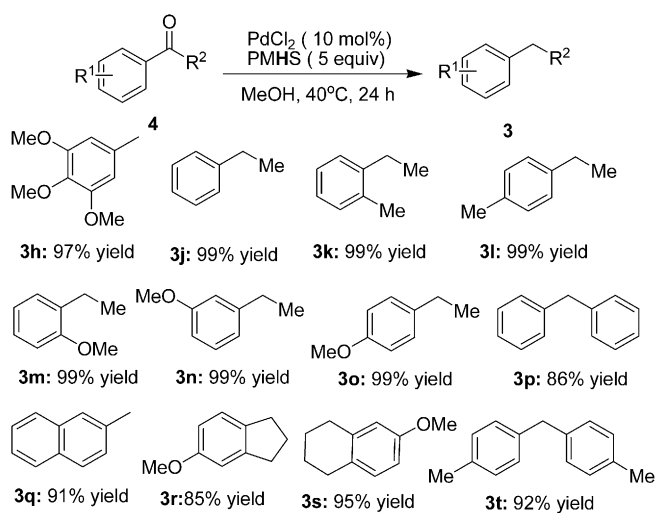
Entry	Alcohol	Product	Time [h]	Yield [%]
8			24	99
9			18	99
10			12	99
11			12	99
12			12	86
13			12	74
14			12	88
15			24	98
16			24	98
17			18	99
18			18	99
19			18	89

^[a] Reaction conditions: benzylic alcohols (1 mmol), PMHS (3 equiv.), PdCl_2 (5 mol%), in MeOH (2 mL), at 40 °C. The isolated yields given in this table are the average values of three runs.

important information for the mechanistic process of palladium-catalyzed reductive deoxygenation, especially the by-product of methyl ether supported that the possible nucleophilic addition of methanol had occurred in the transformation step of the key inter-

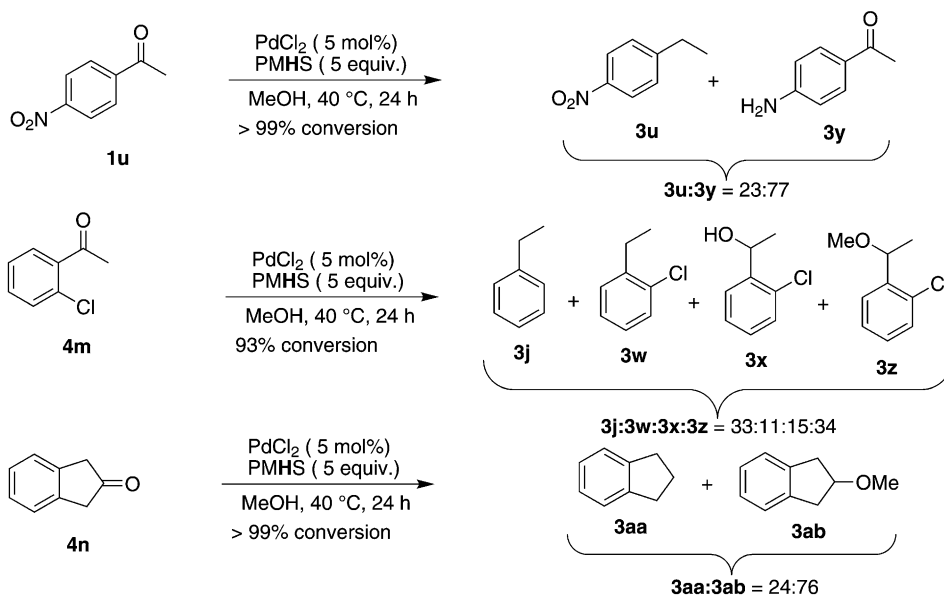


Scheme 3.

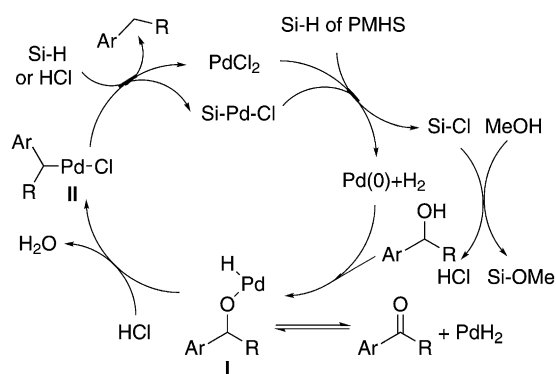


Scheme 4. Reductive deoxygenation of aromatic ketones by palladium in the presence of PMHS.

Scheme 6.



Scheme 5.

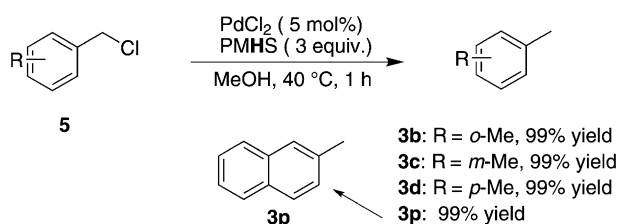


Scheme 7. Possible explanation for the palladium-catalyzed reductive deoxygenation of aromatic alcohols and ketones.

mediate. In addition, even though we did not examine all aromatic ketones containing reducible functional groups, such as amide, cyano, ester, carboxylic acid, sulfoxide, alkenyl, or alkynyl moieties, we evaluated the reactivity of these functional groups in this reduction. Except for alkenyl and alkynyl moieties, amide, cyano, ester, carboxylic acid, and amine (for example, 1-phenylethanamine) were stable and tolerated under the reaction conditions. Also sulfoxide and epoxide groups were reduced partially to sulfanes (see the Supporting Information).

It should be noted that benzylic ethers were successfully converted to the corresponding alkanes *via* C–O cleavage with complete conversion (Scheme 6). We also found that tertiary alcohols were converted to the corresponding alkanes easily under the same reaction conditions (Scheme 6), and the reduction was not limited to benzylic alcohols and ketones, allylic or propargylic alcohols were suitable substrates in this reaction (see the Supporting Information).

Although the mechanistic details of the palladium-catalyzed deoxygenation of ketones or alcohols are not yet clear, we envisaged the pathway of palladium-catalyzed reductive deoxygenation to proceed in two steps on the basis of experimental data. In the first step, we assumed that the palladium-catalyzed hydrosilylation of aromatic ketones or oxidative addition of Pd(0) to benzylic alcohols has occurred, respectively. Then hydrogenolysis of the benzylic alcohol with the aid of the PMHS/PdCl₂ system took place to yield the corresponding chloride or halogenated palladium intermediate that was easily reduced to the hydrocarbons in the presence of a hydrogen source.^[14] A postulated catalytic cycle for representative alcohols is shown in Scheme 7. Initially, the PdCl₂ would be reduced to metallic Pd(0)^[14,15] with the aid of PMHS, which was supported by the evolution of H₂. The by-product of halogenated PMHS containing an Si–Cl moiety could readily react with methanol (solvent) to provide traces of HCl. Then, the benzylic alcohol would add oxidatively to Pd(0) to generate palladium



Scheme 8.

hydride intermediate (**I**). If toluene was used as solvent instead of methanol, a trace of ketone was detected as major by-product (see the Supporting Information), which suggests that the step of oxidative addition was possible. In the key step, the HCl generated from PdCl₂ and PMHS in MeOH facilitates the formation of alkane through a possible chloride intermediate or corresponding halogenated palladium intermediate (**II**). Scheme 8 shows that the reduction of benzyl chloride was easy in the presence of the PdCl₂/PMHS system and indicated that the reductive deoxygenation of alcohols or ketone *via* a chloride intermediate was reasonable. In addition, to elucidate the hydrogen source of the alkane in the reductive deoxygenation, a deuterium incorporation experiment was carried out. When deuterium-labelled methanol (CD₃OD) was used as a solvent in this reaction, a 52% deuterium incorporation was detected (see the Supporting Information), which showed that the hydrogen of the alkane could come from methanol by hydride transfer between intermediate **I** and solvent. However, it is hard to draw a final conclusion to exclude the presence of a carbocation intermediate^[16] in the last step because the methyl ether products, for example, 4-(1-methoxyethyl)benzenamine or 1-chloro-2-(1-methoxyethyl)benzene was detected, respectively, in the deoxygenated reaction of 1-(4-nitrophenyl)ethanol and 1-(2-chlorophenyl)ethanone (Scheme 3 and Scheme 5).

In summary, we have demonstrated a new application of palladium as reductive deoxygenation catalyst for the reduction of aromatic ketones and benzylic alcohols in the presence of PMHS. The reductive deoxygenation of aromatic ketones and benzylic alcohols, including secondary alcohols to the corresponding methylene hydrocarbons has been achieved in good to excellent yields by PdCl₂ catalyst and PMHS as hydride source. Such deoxygenations were successfully achieved with aryl ketones and diaryl ketones, as exemplified by the reductive deoxygenation of acetophenone and benzophenone, respectively. The corresponding benzylic alcohols and secondary alcohol analogues could also be converted into their respective methylene hydrocarbons by PdCl₂/PMHS system. Although the mechanistic details of the palladium-catalyzed deoxygenation of ketones or alcohols are not yet clear, the method is of importance and utility in

organosilicon and basic organic chemistry due to the improved synthesis of various alkanes as demonstrated in this article.

Experimental Section

General Remarks

All reaction flasks and solvent were used directly. The hydrogenated silicone [viscosity (25 °C), mm²/MS: 10–50; hydroxyl content: 1.55–1.60; density (25 °C), g cm⁻³: 0.995–1.015] was purchased from Cheng xing County Chemical Co., Ltd., (Zhejiang, China Chinatown Kaihua). Other reagents are commercially available and used directly without further purification. Flash column chromatography was performed over silica (200–300 mesh). ¹H NMR and ¹³C NMR spectra were recorded at 400 and 100 MHz, respectively, on an Advance (Bruker) 400 MHz nuclear magnetic resonance spectrometer, and were referenced to the internal solvent signals. Thin layer chromatography was performed using silica gel; GF254 TLC plates and visualized with ultraviolet light. The products of the reductive deoxygenation reaction were known and confirmed by GC-MS, and the usual spectral methods (¹H NMR).

General Procedure for Reductive Deoxygenation of Aromatic Ketones or Benzylic Alcohols

Under a nitrogen atmosphere, the benzylic alcohol or aromatic ketone (1 mmol) was added to a dry tube containing PdCl₂ (5 mol% or 10 mol%), PMHS (0.2 mL: 3 equiv. for alcohols or 0.34 mL: 5 equiv. for ketones, calculated on the hydrogen content of Si–H) and methanol (2 mL). And then the mixture was stirred at 40 °C for 12–24 h. After the completion of the reaction, the product was dissolved in *n*-hexane, the reaction course was monitored by GC-MS or TLC. The combined organic layers were dried (Na₂SO₄), concentrated under vacuum, and purified by column chromatography on silica gel to gain the pure product. All the products are confirmed by GC-MS, NMR, and IR, and representative characterization data for products **3** are listed in the Supporting Information.

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