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Suman Pramanik, Anthony Fernandes, Virginie Liautard, Mathieu Pucheault, Frédéric Robert, et al.. Dehydrogenative Silylation of Alcohols Under Pd-nanoparticles Catalysis. Chemistry - A European Journal, 2019, 25 (3), pp.728-732. 10.1002/chem.201803989 . hal-02012175

HAL Id: hal-02012175

<https://hal.science/hal-02012175>

Submitted on 8 Feb 2019

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Dehydrogenative Silylation of Alcohols Under Pd-nanoparticles Catalysis.

Suman Pramanik,[a] Anthony Fernandes,[a] Virginie Liautard,[a] Mathieu Pucheault,[a] Frederic Robert*[a] and Yannick Landais*[a]

Abstract: *Pd-nanoparticles catalyzed dehydrogenative coupling between various hydrosilanes and alcohols was shown to provide silyl ethers in good and reproducible yields. The synthetic methodology is effective for a wide range of simple and bulky silanes and secondary alcohols, while keeping various other functional groups intact. The procedure also exhibits high selectivity for the silylation of primary versus secondary alcohols in 1,2-diols, and allows the successive silylation of alkynols and hydrogenation of the triple bond to afford Z-alkenols in good yields.*

Silyl ether compounds have attracted much attention in material science.[1] Protection of alcohols through silylation is well-known in organic synthesis and is frequently used in the preparation of synthetic materials[2] and in total synthesis of natural products.[3] Hydrolytic silylation is an invaluable tool for the production of functionalized mesoporous silica nanospheres through grafting or co-condensation processes.[4] The protection of alcohols and phenols with silyl groups significantly changes their thermal stability and polarity. Additionally, trimethylsilyl derivatives are thus often prepared from free alcohols for GC analysis purposes, due to a lower polarity and a higher volatility than the parent alcohols.[5] The high demand for silyl ethers thus continuously attracts interest among organic chemists for their synthesis.[6-8] The silylation of alcohols is commonly performed by the use of silyl chlorides in the presence of base, producing equimolar amount of hydrochloride salts.[6] To circumvent the frequent lack of efficiency for the protection of sterically hindered or less reactive alcohols, silyl triflate reagents are generally required.[7] However, the latter suffer from moisture sensitivity and high costs. Recently, considerable attention has been paid to the construction of Si-O bond through catalytic dehydrogenative silylation of alcohols.[8] This alternative method is based on the use of hydrosilanes under neutral conditions, producing H₂ as the sole by-product (Scheme 1). Although this atom economical approach has considerable importance, the coupling process using non-toxic and hydrolytically more stable silicon reagents, catalysts used in these reactions are incompatible for both sterically hindered silanes and alcohols in many instances. The rate of B(C₆F₅)₃-catalyzed dehydrogenative coupling is for instance controlled by the steric factor of the hydrosilane.[9] Reported dehydrogenative silylation reactions either involve bulky silane or secondary alcohols as coupling partners.[8,10] The development of new methods for dehydrogenative silylation, irrespective of the nature of the silane and the alcohol, is in demand,[11,12] with applications in diverse fields including material science,[13] functional polymers,[14] and organocatalysis.[15]

During the past two decades, Pd nanoparticle (Pd-NP) catalysts have attracted significant attention due to their wide applicability in the field of coupling reactions forming C-C bond,[16] alkene hydrogenation,[17] reduction of aromatic nitro compounds,[18] and α -allylic substitution reactions.[19] Transformation of hydrosilanes into silanols in the presence of water has been reported using carbon-supported or aluminium oxy-hydroxide-supported Pd-NP catalysts (Scheme 1).[20] Dehydrocoupling of hydrosilanes with methanol or ethanol has been developed by utilizing dealloyed

nanoporous Pd catalysts.[21] The exploration of new catalytic methods based on supported nanoporous Pd-catalysts continues to be beneficial in addressing remaining challenges in dehydrogenative coupling reactions.

Catalytic dehydrocoupling

- Either the silane or alcohol is sterically crowded

Pd-nanoparticle (Pd-NP) catalyzed dehydrogenative silylation

- H₂O, MeOH or EtOH as the coupling partner

This Work

- Both hydrosilane and alcohol may be sterically crowded

Scheme 1. Catalytic dehydrogenative silylation.

During our continuous studies on the reactivity of organosilicon compounds and derivatives,[22] we experienced some difficulties for the synthesis of sterically crowded silyl ethers using reported literature procedures. Therefore, we were looking for a catalytic system which would be tolerant to steric hindrance, allowing for the dehydrogenative silylation of bulky secondary alcohols with various silanes. Recent studies by one of us on the use of montmorillonite, Layer Double Hydroxides (LDH), oxides or carbon as a solid supports, showed these catalysts to be highly reactive in a wide range of transformations, indicating that they might suit our purpose.[23] Herein, we report the development of a convenient dehydrocoupling reaction between hydrosilanes and alcohols with various steric demands, leading to the corresponding silyl ethers, using Pd-NP. Yields are generally good, the procedure allowing various substituents on the silicon center. The procedure has good functional group tolerance, including Lewis basic moieties and exhibits excellent selectivity in 1,2-diol monoprotection.

(-)-Menthol 1a and sterically hindered carbazole substituted hydrosilane 2a were chosen as model substrates for dehydrogenative coupling reaction, illustrating notably a relatively high steric hindrance around silicon. All standard methods to access 3a proceeding through the silyl chloride or triflate analogues of 2a failed before. Several Pd-NP based catalysts were used in our study.[24] The Pd-NP were formed by borane reduction of palladium(II) Chloride in the presence of the solid support, namely Kunipia MMT, K10 MMT or DARCO Charcoal: Pd-NP1 was thus obtained through reduction of PdCl₂ using NaBH₄ in the presence of Kunipia MMT, Pd-NP2 using diisopropylamine-borane (DIPAB) complex and Kunipia MMT, Pd-NP3 using NaBH₄ and K10 MMT, and Pd-NP4 using NaBH₄ and DARCO carbon (See supporting information, SI). We began our investigations with Pd-NP1 catalyst in n-dibutylether as a solvent. The dehydrocoupled product 3a was obtained in an encouraging 50% yield (Table 1, entry 1). A survey of catalyst screening showed that Pd-nanoparticle catalysts Pd-NP2 and Pd-NP3 gave respectively moderate to low yield of the desired product (entry 2 and 3, Table 1). Carbon-supported Pd catalyst Pd-NP4 showed similar catalytic activity than MMT-supported Pd catalyst Pd-NP1, affording

the desired dehydrocoupled product in 53% yield. As the carbon-based catalyst was easier to remove by filtration, it was designated as the catalyst of choice for further studies (entry 4). X-ray Photoelectron Spectroscopy (XPS) analysis showed that most of the palladium was under the form of Pd(0) (70%), the remaining being PdO (30%), probably as a result of the oxidation of Pd(0) by air during the XPS analysis. The metal loading was found to average between 0.3 to 0.35% depending on sample. We further tested various solvents including THF, t-butyl methylether, n-hexane and n-heptane (entry 5 to 8) and found that n-dibutylether was the most suitable for the reaction. Finally, when the reaction was heated for 24 h at 70 °C in the presence of Pd-NP4 catalyst, the yield was improved to 56% (entry 9), which corresponds to a TON of 662. Although yield is still moderate, it is noteworthy that all standard methods to access 3a failed. Finally, other attempts such as increasing temperature did not improve the yield further.

Table 1. Optimization of the dehydrogenative silylation of menthol.

Entry ^[a]	Catalyst ^[b]	Solvent	Yield [%] ^[c]
1	Pd-NP1	<i>n</i> Bu ₂ O	50
2	Pd-NP2	<i>n</i> Bu ₂ O	44
3	Pd-NP3	<i>n</i> Bu ₂ O	12
4	Pd-NP4	<i>n</i> Bu ₂ O	53
5	Pd-NP4	THF	8
6	Pd-NP4	MTBE	17
7	Pd-NP4	<i>n</i> -hexane	21
8	Pd-NP4	<i>n</i> -heptane	23
9 ^[d]	Pd-NP4	<i>n</i> Bu ₂ O	56 (54) ^[e]

[a] Reaction Conditions: **1a** (0.5 mmol), **2a** (1.5 equiv., 0.75 mmol), Pd-catalyst (15 mg) in solvent (2 mL) at 70 °C for 16 h. [b] **Pd-NP1**: PdCl₂/NaBH₄/MMT Kunipia; **Pd-NP2**: PdCl₂/Pr₂NH-BH₃/MMT Kunipia; **Pd-NP3**: PdCl₂/NaBH₄/K10 MMT; **Pd-NP4**: PdCl₂/NaBH₄/DARCO carbon. Reduction of PdCl₂ (1 mmol) is performed over 1 g of solid support (MMT or Charcoal) in MeOH. [c] Yield was calculated from the ¹H NMR of the reaction mixture using mesitylene as internal standard. [d] 2.5 equiv. of silane was used and the reaction heated for 24 h. [e] Isolated yield after column chromatography.

With these optimized reaction conditions in hand, the methodology was extended to a variety of hydrosilanes using Pd-NP4 as the catalyst (Table 2). Hydrosilanes showing various substitutions patterns, including aryl and alkyl groups are well tolerated (Table 2, entry 2-3). The silylation of (-)-menthol with triphenylsilane afforded the corresponding silyl ether 3d in high yield (entry 4). The reaction proceeded at 100 °C in the presence of tert-butyl substituted hydrosilanes 2e and 2f which are bulkier than arylsilanes (entry 5 and 6), affording moderate yields of silyl ethers.

Table 2. Scope of hydrosilanes for dehydrocoupling.

Entry ^[a]	Silane	R ¹	R ²	R ³	Time (h)	Yield [%] ^[b]
1	2a	Carbazole	Ph	Me	46	3a 54 ^[c] (d.r. 1:1)
2	2b	Ph	Me	Me	16	3b , 85
3	2c	Et	Et	Et	20	3c , 97
4	2d	Ph	Ph	Ph	20	3d , 81
5	2e	Ph	^t Bu	Me	46	3e 43 ^[c] (d.r. 1:1)
6	2f	^t Bu	Me	Me	42	3f , 47 ^[c]
7	2g	Cyclohexyl	Me	Me	21	3g , 93

[a] Reaction Conditions: **1a** (0.5 mmol), **2** (2.5 equiv., 1.25 mmol), Pd-catalyst (15 mg, 0.42 μmol), in tBu_2O (2 mL) at $70\text{ }^\circ\text{C}$. [b] Isolated yield after column chromatography. [c] 30 mg of catalyst was used instead of 15 mg and heated at $100\text{ }^\circ\text{C}$ instead of $70\text{ }^\circ\text{C}$.

Cyclohexyldimethylsilane (**2g**) reacted smoothly to furnish the desired silyl ether in high yield (entry 7). Our Pd-NP catalytic method thus leads to dehydrogenative silylation of (-)-menthol with various hydrosilanes in moderate to excellent yields depending on the steric hindrance of the starting silane.

After successful synthesis of silyl ethers from (-) menthol, the scope of the transformation was further investigated, varying the nature of the alcohol partner **1** using Ph_3SiH (Scheme 2). Sterically crowded (-) borneol was shown to afford the silyl ether **3h** when reacting with triphenyl silane over a longer period of time. Small and medium-sized secondary aryl alcohols were amenable to the Pd-nanoparticle catalyzed dehydrocoupling reactions to give the silyl ethers **3i** and **3j** in excellent yields. It is noticeable that Pd-catalyzed debenzylation did not occur with benzylic alcohols and ethers (i.e. **3i**). Cyclic secondary and tertiary alcohols were also tested, 4-tertbutylcyclohexanol and 1-adamantanol being found equally effective, providing the corresponding dehydrocoupled product **3k-l**. Selective coupling with alcohols in the presence of fragile or reducible ester and chloro functionalities also showed the efficiency of the current protocol to furnish **3m-o**. The feasibility of our method was further manifested with naturally occurring 5α cholestan 3β ol that was silylated to give **3p** under our reaction conditions.

[a] Reaction at 100 °C using 60 mg/mmol catalyst.

Scheme 2. Scope of the dehydrogenative silylation of alcohols

When the above procedure was applied to propargylic alcohols, protection of the OH groups was observed, along with the hydrogenation of the triple bond (Scheme 3). Catalytic access to thermodynamically less stable Z-alkenols was thus achieved by tandem dehydrogenative silylation/hydrogenation of propargyl alcohols or homopropargyl alcohols. It provides an atom economical process for both the dehydrocoupling and hydrogenation reactions using in-situ generated H₂. Aryl and alkyl substituted allyl silyl ethers (**3q** and **3r** respectively) were synthesized directly from propargyl alcohols in good yields. Homopropargyl alcohols also provided the homoallyl silyl ethers in this reaction (**3s**). Selectivity in favour of the Z-alkene was not influenced by the nature of the silyl protecting group. The length of the carbon chain between the triple bond and the alcohol function has no major influence on the process as shown by the formation of alkoxysilane **3t**.

Scheme 3. Tandem dehydrogenative silylation/hydrogenation of alkynols.

In addition, selectivity between primary and secondary alcohols was examined (Scheme 4). Homochiral 1-phenylethane-1,2-diol was reacted with 1.0 and 2.0 equivalents of dimethyltert-butylsilane under standard reaction conditions. Although our methodology is efficient for the silylation of secondary benzylic alcohols (as mentioned in Scheme 2), an excellent selectivity was observed towards primary

alcohol even in the presence of excess hydrosilane. Optical rotation of silyl ether 5a proved to be in excellent agreement with that reported in the literature,[25] indicating that the dehydrogenative silylation of benzylic 1,2-diols is not only regioselective, but also occurs with no erosion of the chirality at the benzylic center. Competition between secondary and tertiary alcohols in diol 4b, using a smaller hydrosilane, led to the sole protection of the secondary hydroxy group (i.e. 5c), albeit requiring an excess of the silane to obtain high yield.

Scheme 4. Selectivity for the silylation between 1°, 2° and 3° alcohols.

Finally, silyl ethers may also be obtained through a tandem ring opening-silylation of epoxides using our catalysts.[26] Silyl ether 7 was thus prepared in good yield through the epoxide ring opening of styrene oxide 6 in the presence of $t\text{Bu}_2\text{SiH}_2$, illustrating the versatility of these readily available catalysts (Scheme 5).

Scheme 5. Silylation of epoxides.

In conclusion, we have developed a practical method for the dehydrogenative coupling between various types of hydrosilanes and alcohols. This Pd-nanoparticle catalyzed method offers significant advantages over the previous protocols for the synthesis of sterically hindered silyl ethers. It allows the reaction to be performed under mild neutral conditions, without the recourse to strong bases ($t\text{BuOK}$ or KOH for instance), using cheap and readily prepared catalysts. The method offers good compatibility with various functional groups, such as chlorides, esters and benzylic alcohols and ethers. Examples for the synthesis of allyl and homo-allylsilyl ethers from propargyl and homopropargyl alcohols in an atom economical tandem silylation-hydrogenation process were also provided to demonstrate the utility of the process. This synthesis of silyl ethers uses readily available starting materials and Pd-nanoparticles which are easily accessible. It is thus anticipated that this approach should find applications in organic synthesis.

Experimental Section

General procedure for the dehydrogenative silylation

In a sealed tube equipped with a magnetic stir bar, was placed (-)-menthol (78 mg, 0.5 mmol). It was introduced into a glove box and 15 mg of Pd-nanoparticle catalyst was added. The tube was capped and taken out from the glove box. Anhydrous n-dibutylether (1.5 mL) (distilled over Na) was added via syringe followed by the addition of a solution of triphenylsilane (2.5 equiv., 1.25 mmol) in n-dibutylether (0.5 mL). The reaction mixture was heated to 70 °C until starting material is consumed. After the reaction is completed, the crude mixture was filtered through a short plug of silica to remove Pd-catalyst eluting with dichloromethane. Following evaporation of the solvents under vacuum, flash column chromatography was performed on silica gel using ethyl acetate in petroleum ether to get the desired product (168 mg, 81% yield).

Acknowledgements

SP thanks EU for a postdoctoral grant through H2020-MSCA-IF-2015 program (N° 704870). The Agence Nationale de la recherche is thanked for financial support through program (ANR-16-CE07-0018-01). The University of Bordeaux and CNRS are gratefully acknowledged for financial support.

Keywords: dehydrogenative silylation • hydrosilane • Pd nanoparticles • protecting group • hydrogenation

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