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Nonhydrolytic Synthesis of Silanols by the Hydrogenolysis of Benzyloxysilanes

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The hydrogenolysis of benzyloxysilanes was smoothly catalyzed by Pd/C in THF to give corresponding silanols under nonhydrolytic conditions. The reaction proved to be applicable to various benzyloxysilanes giving silanemonools, diol, and triol.

Silanols are important chemical species that are widely used as building blocks for silicon-based polymeric materials and are also important intermediates generated from halosilanes and alkoxysilanes in sol–gel-type processes.[1,2] They are also used as reagents and catalysts in organic synthesis; aryl-, alkenyl-, and alkynylsilanols are useful cross-coupling reagents[3] and silane diols and bis(silanols) are new types of organocatalysts based on their strong hydrogen-bonding formation.[4] Extensive hydrogen-bonding networks formed by silanols would also be useful as building blocks for supramolecular organometallic chemistry.[5] Introduction of a silanol moiety in a molecule attracts considerable interests in medicinal chemistry.[6]

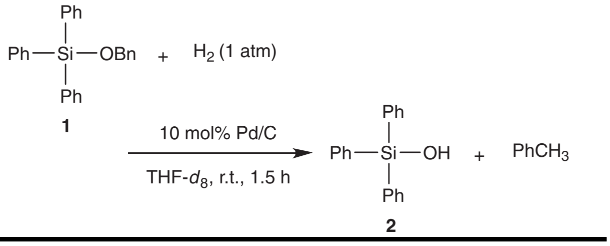
Two methods are mainly used for the preparation of silanols. One is hydrolysis of compounds containing Si–X groups such as chlorosilanes and alkoxysilanes.[2] The resulting silanols are often further condensed without isolation to form oligomeric and polymeric materials. This process is very important in the silicone industry. The other general method is the oxidation of hydrosilanes using oxidizing agents, such as dioxiranes.[2] This oxidation method is mostly limited to the preparation of silanemonools. Recently, highly efficient catalysts for the oxidation of hydrosilanes using water as an oxidant have been developed.[7]

Sterically less demanding silanols are difficult to isolate because they easily condense to form siloxanes, in particular upon concentration. As mentioned above, most silanol syntheses are conducted in the presence of water. Therefore, it is difficult to use the resulting silanols for reaction with moisture-sensitive compounds such as halosilanes and metal alkoxides, if the silanols cannot be isolated. We are interested in developing nonhydrolytic preparation of silanols, so that they can be directly used for reaction with moisture-sensitive compounds. Herein, we report nonhydrolytic synthesis of silanols by the Pd/C-catalyzed hydrogenolysis of benzyloxysilanes.

Benzyl ethers are commonly used to protect hydroxy groups in organic syntheses.[8] The benzyl groups can be readily removed by hydrogenolysis catalyzed by Pd/C. However, this procedure is rarely used for the protection of silanols.[9] We thought this procedure is useful for the nonhydrolytic synthesis of silanols. The starting materials, benzyloxysilanes, can be prepared by the reaction of corresponding chlorosilanes with benzyl alcohol in the presence of triethylamine and a catalytic amount of 4-(dimethylamino)pyridine.[10]

Commercially available Pd/Cs are generally sold moistened with water for safety. Sajiki and Hirota reported that residual acids of Pd/Cs (depending of suppliers) cause solvolytic cleavage of silyl ethers.[11] Thus, in order to avoid hydrolytic cleavage of benzyloxysilanes, all Pd/Cs used in this study were dried by heating at 120 °C for 48 h under vacuum before use.

Table 1. Hydrogenolysis of **1** using various types of Pd/Cs[a]



Entry	Pd/C (wt %)	Conv. /%[b,c]	Yield /%[d]	Selectivity /%[e]
1	OH type (Pd 10 wt %)	8	6	75
2	ASCA-2 (Pd 4.5 wt %, Pt 0.5 wt %)	98	95	97
3	PE type (Pd 10 wt %)	14	13	93
4	NX type (Pd 5 wt %)	8	6	75

[a]Reaction conditions: **1** (0.150 mmol) and Pd/C (10 mol %) were stirred under hydrogen atmosphere (1 atm) at room temperature for 1.5 h in THF-d_8 (1.0 mL). [b]Convresion of Ph_3SiOBn. [c]Conversion and yield based on **1** were determined by integration of ^{29}Si NMR spectra using inverse-gated decoupling pulse sequence with 1,4-bis(trimethylsilyl)benzene as an internal standard. [d]Yield of Ph_3SiOH. [e]Selectivity = Yield/conversion (%).

Initial attempts by using OH-type Pd/C (N. E. CHEMCAT), which is recommended for the deprotection of benzyl ethers by the supplier, proved that it was not a very effective catalyst for the deprotection of Ph_3SiOBn (Bn: benzyl) (**1**) (Table 1, Entry 1). Therefore, we surveyed several other types of Pd/Cs available from the same supplier for the reaction. The hydrogenolysis of **1** was conducted by stirring a mixture of **1** (0.150 mmol) and Pd/C (10 mol %) in THF-d_8 (1 mL) under 1 atm of H_2 at room temperature for 1.5 h in a sealed tube. As shown in Table 1, ASCA-2 (N. E. CHEMCAT), which contains Pt (0.5 wt %) and Pd (4.5 wt %), completed the deprotection of **1** within 1.5 h (95% yield and 97% selectivity, Table 1, Entry 2). Simultaneous generation of an approximately equimolar amount of toluene (93%) was confirmed by ^{1}H and ^{13}C NMR spectra of the reaction mixture. Other Pd/Cs, PE- and NX-types (N. E. CHEMCAT), which are also recommended for benzyl ether deprotection, are also much less effective than ASCA-2 (Table 1, Entries 3 and 4).

Table 2 summarizes the solvent effects in this reaction by using ASCA-2-type Pd/C as a catalyst. THF is the solvent of choice in this reaction, giving the desired product nearly quantitatively within 1.5 h at room temperature (Entry 2). On the other hand, in the other five solvents, MeCN, CH_2Cl_2, EtOAc, toluene, and hexane, the reaction proceeded slowly with lower selectivities. The reason of this specific preference for THF is not clear at the moment.

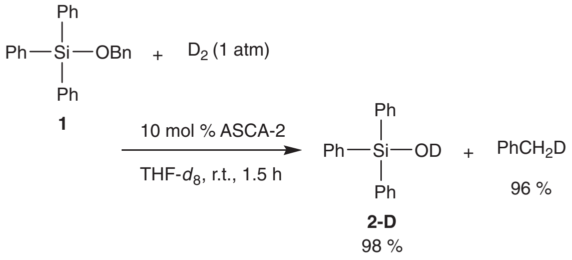
The deprotection reaction of **1** did not proceed in the absence of H_2 or the catalyst at all. The hydrogenolysis of **1** catalyzed by Pd/C (ASCA-2) was further confirmed by the experiment using D_2 instead of H_2 (Scheme 1). Treatment of **1** under 1 atm of D_2 at room temperature for 1.5 h in the presence of ASCA-2 (10 mol %) in anhydrous THF-d_8 almost quantitatively afforded the expected products Ph_3SiOD and $PhCH_2D$ (respectively 98% and 96% by NMR).

Table 2. Solvent effect toward the hydrogenolysis of **1**[a]

Entry	Solvent	Conv. /%	Yield /%[b]	Selectivity /%[c]
1	MeCN	18	11	61
2	THF	98	95	97
3	CH_2Cl_2	19	16	84
4	AcOEt	20	18	90
5	Toluene	13	8	62
6	Hexane	11	8	73

[a] Reaction conditions: **1** (0.150 mmol) and Pd/C (ASCA-2 type, 10 mol %) were stirred under hydrogen atmosphere (1 atm) at room temperature for 1.5 h in various solvents (1.0 mL). [b] Conversion and yield based on **1**, were determined by integration of ^{29}Si NMR spectra using inverse-gated decoupling pulse sequence with 1,4-bis(trimethylsilyl)benzene as an internal standard. [c] Selectivity = Yield/conversion (%).

This nonhydrolytic procedure is well applicable to various benzyloxysilanes (Table 3).[12] Not only arylsilanes, but also an alkylsilane, *i*-Pr_3SiOBn, efficiently converted to the corresponding silanol (Table 3, Entry 2). Replacement of one or two Ph groups of **1** with Me groups considerably affected the selectivities partly because of the ease of self-condensation to form disiloxanes (Table 3, Entries 3 and 4). Sajiki and Hirota reported that a solution treated with Pd/Cs (depending on suppliers) under H_2 became acidic due to the residual acids and/or $PdCl_2$ in Pd/Cs.[11] Therefore, it is possible that the acid coming from Pd/C accelerates self-condensation of silanols. In Entry 4, yield of silanol considerably decreased (4%). This is probably attributed not only to the acceleration of silanol condensation but also to the adsorption of silanol on Pd/C, because total recovery of products was considerably low in this case. Actually, reduction of the catalyst amounts from 10 to 1 mol % considerably increased the silanol yield from 4 to 51% and slightly decreased the disiloxane yield from 55 to 44%



Scheme 1. Deuteriolysis of **1** with D_2.

Table 3. Hydrogenolysis of various benzyloxysilanes using Pd/C (ASCA-2 type)[a]

$$R_{4-n}Si(OBn)_n + H_2\text{ (1 atm)} \xrightarrow[\text{THF-}d_8]{\text{ASCA-2}} R_{4-n}Si(OH)_n + \{R_{4-n}(HO)_{n-1}Si\}_2O + n\ PhCH_3$$

$n = 1, 2, 3$

Entry	Benzyloxysilane	Pd/C (mol % Pd for each benzyloxy group)	Temp. /°C	Time /h	Conv. /%	Yield/%[b] $R_{4-n}Si(OH)_n$	Yield/%[b] $\{R_{4-n}(HO)_{n-1}Si\}_2O$	Selectivity /%[c]
1	Ph_3SiOBn	10	r.t.	1.5	98	95 (90)	0	97
2	*i*-Pr_3SiOBn	10	r.t.	1.5	100	82	0	82
3	$Ph_2MeSiOBn$	10	r.t.	1.5	100	60	13	60
4	$PhMe_2SiOBn$	10	r.t.	1.5	100	4	55	4
5		1	r.t.	1.5	100	51	44	51
6		1	−25	1.5	86	66	17	77
7	Ph_2*t*-BuSiOBn	10	r.t.	1.5	24	19	0	79
8		10	r.t.	20	74	69	0	93
9		10	r.t.	40	85	80	0	94
10	$Ph_2ViSiOBn$[d]	10	r.t.	1.5	100	70[e]	5	70
11[f]	$Ph_2Si(OBn)_2$	10	r.t.	1.5	100	58	0	58
12		5	r.t.	1.5	98	89	5	91
13	$PhSi(OBn)_3$	1	r.t.	1.5	85	22	54	26
14		3	−25	1.5	90	32	40	36

[a] Reaction conditions: Benzyloxysilane (0.150 mmol) and Pd/C (ASCA-2 type) were stirred under hydrogen atmosphere (1 atm) in THF-d_8 (1.0 mL). [b] Conversion and yield based on each benzyloxysilane were determined by integral value of ^{29}Si NMR analysis using inverse-gated decoupling pulse sequence with 1,4-bis(trimethylsilyl)benzene as an internal standard. The values in parentheses show the yield of isolated product. [c] Selectivity = Yield of $R_{4-n}Si(OH)_n$/conversion (%). [d] Vi: vinyl. [e] The product is $Ph_2EtSiOH$. [f] $Ph_2Si(OBn)_2$ (0.075 mmol) was used.

(Table 3, Entries 4 and 5). Furthermore, the selectivity to $PhMe_2SiOH$ increased to 77% by conducting the reaction at lower temperature, −25 °C (Table 3, Entry 6). Introduction of a bulkier substituent, *t*-Bu, to **1** considerably decreased the conversion under the same reaction conditions (24% conversion and 19% silanol yield, Table 3, Entry 7). As expected, longer reaction time increased the conversion (74% after 20 h and 85% after 40 h, Table 3, Entries 8 and 9) while keeping good selectivity. In the case of a vinyl-substituted compound, hydrogenation of the vinyl group simultaneously took place to give $Ph_2EtSiOH$ (Table 3, Entry 10). This methodology can also be applied to the synthesis of silanediol and -triol, although condensation of the resulting silanols to the dimers and higher oligomers becomes more serious. Thus, in the case of $Ph_2Si(OBn)_2$, decreasing the catalyst amounts from 10 mol % to 5 mol % increased the yield and the selectivity of $Ph_2Si(OH)_2$ respectively from 58% to 89% and from 58% to 91% (Table 3, Entries 11 and 12). It was difficult to suppress the condensation to the siloxanes in the case of $PhSi(OBn)_3$ by reducing the catalyst amounts and/or by lowering the reaction temperature; 1 mol % of the catalyst at room temperature or 3 mol % of the catalyst at −25 °C respectively resulted in 26% and 36% selectivities to $PhSi(OH)_3$ (Table 3, Entries 13 and 14).[13]

In summary, we found a versatile and effective Pd/C-catalyzed hydrogenolysis of benzyloxysilanes to the corresponding silanols under nonhydrolytic mild conditions. This synthetic method is applicable to the synthesis of silanemonools, -diol, and -triol. Further study to improve the selectivity as well as the application of this procedure for the reaction with moisture sensitive compounds, such as halosilanes and metal alkoxides, is underway in our laboratory.

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12 General procedure for the hydrogenolysis of benzyloxysilane: A stirred mixture of the benzyloxysilane (0.150 mmol) and Pd/C (0.2–10 mol % Pd for each benzyloxy group) in THF-d_8 (1.0 mL) was treated with hydrogen gas (1 atm) at room temperature for an appropriate time. The reaction mixture was filtered through a membrane filter (GE Healthcare Puradisc 13, 0.45 µm) to remove the catalyst. 1,4-Bis(trimethylsilyl)benzene as an internal standard for NMR analysis and a trace amount of $[Cr(acac)_3]$ as a relaxation agent were added to the filtrate. The mixture was subjected to ^1H and ^{29}Si NMR (inverse-gated decoupling pulse sequence) analysis to determine the conversion and the yield. The details of the quantitative ^{29}Si NMR analysis are shown in the Supporting Information.[13]

13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.