A Novel Method for Preparing Silanols from Silylmethanols

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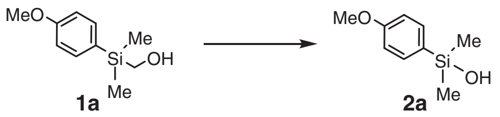
Various types of silylmethanols were converted into their corresponding silanols in good to excellent yield under mild oxidation conditions using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl).

Today, silanol compounds are attracting increased attention because they are valuable building blocks in Pd-catalyzed cross-coupling reactions.[1] Many methods, including hydrolysis of chlorosilanes,[2] oxidation of organosilanes using stoichiometric amounts of oxidants,[3] and reaction of lithium reagents with cyclotrisiloxanes[4] have been developed for preparing silanols. However, the yields obtained in most of the known methods are often low because of formation of siloxanes.[2a,5] Further, some of these methods generate large amounts of environmentally hazardous wastes. Recently, environmentally benign reactions for the oxidation of silanes into silanols have been reported by several groups,[6] these reactions use water as a green oxidant in the presence of metal catalysts. To our best knowledge, however, none of the above-mentioned reactions have been used for the preparation of silanols bearing ester groups or amide groups or carboxylic acids. The only method that can be applied to ester-bearing substrates is Pd-catalyzed silylation of aryl bromides with 1,2-diethoxy-1,1,2,2-tetramethyldisilane and subsequent hydrolysis of the obtained ethyl ethers.[7] Although this method is effective, it requires expensive reagents. Herein, we wish to report a novel method for the preparation of silanols without using expensive or environmentally hazardous reagents. Since our method requires mild conditions, it can be applied to a variety of substrates.

Initially, we found that silylmethanol compounds could be converted into their corresponding silanols under oxidation conditions (Table 1). We investigated the oxidation of [(4-methoxyphenyl)dimethylsilyl]methanol (**1a**) under different conditions. Use of tetrapropylammonium perruthenate (TPAP) with *N*-methylmorpholine *N*-oxide (NMO), the Swern oxidation, and the Dess–Martin reagent resulted in poor yields (Entries 1–3). With sulfer-trioxide pyridine complex (Entry 4) and 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) (Entry 5) we could obtain high yields, and further, only traces of disiloxanes were formed. The synthetic route of **1a** is shown in Supporting Information.[8]

Table 1. Study of oxidation conditions

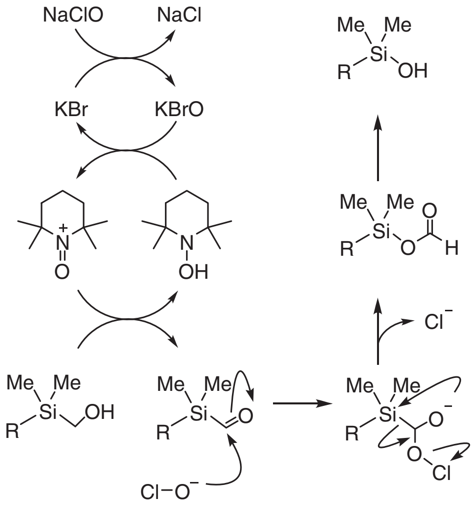


1a **2a**

Entry	Reagents	Solvent	Conditions	Yield[a]/%
1	TPAP (0.1 equiv) NMO (2.5 equiv) MS4AP	CH_2Cl_2	rt, 1.5 h	62
2	$(COCl)_2$ (2.0 equiv) Et_3N (4.0 equiv) DMSO (6.0 equiv)	CH_2Cl_2	−78 °C, 1 h	46
3	Dess–Martin reagent (2.0 equiv)	CH_2Cl_2	rt, 1 h	31
4	SO_3•Py (3.0 equiv) Et_3N (6.5 equiv)	DMSO	rt, 30 min	81
5	TEMPO (0.1 equiv) NaOCl (2.0 equiv) KBr (0.1 equiv)	Acetone aq $NaHCO_3$	rt, 1 h	82

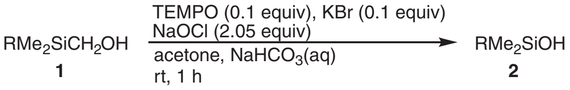
[a]Isolated yield after silica-gel column chromatography.

We extended the silylmethanol–silanol conversion reaction to several substrates (Table 2). Arylsilylmethanols containing both electron-rich and electron-deficient groups were converted into their corresponding silanols in good to excellent yields (Entries 1–3). In those reactions, ester groups were not affected. Halogen-bearing substrates were also successfully converted into corresponding silanols (Entries 4 and 5). Bissilylmethanol was oxidized into its corresponding silanol in excellent yield (Entry 6). A substrate possessing a carboxylic acid group was converted into its corresponding silanol in almost quantitative yield (Entry 7). Dimethyl(2-thienyl)silylmethanol was also successfully converted into its corresponding silanol (Entry 8). However, (3-furyldimethylsilyl)methanol decomposed under the present conditions (Entry 9); this might be due to the low stability of the furan ring under oxidation conditions.[9] A general experimental procedure and spectroscopic data of silanols are shown in Supporting Information.[8]

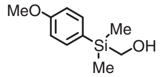
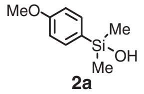
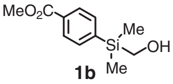
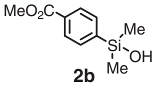
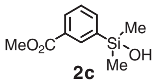
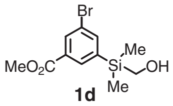
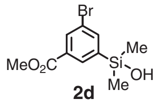
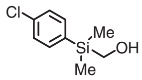
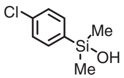
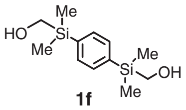
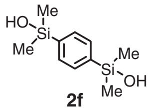
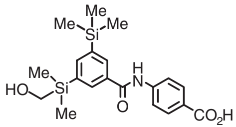
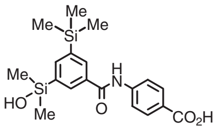
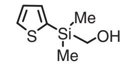
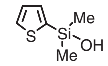
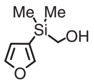
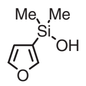


Scheme 1. Plausible mechanism for the silylmethanol–silanol conversion.

Table 2. Silylmethanol–silanol conversion



$$\underset{\mathbf{1}}{\mathrm{RMe_2SiCH_2OH}} \xrightarrow[\text{acetone, NaHCO}_3\text{(aq), rt, 1 h}]{\text{TEMPO (0.1 equiv), KBr (0.1 equiv), NaOCl (2.05 equiv)}} \underset{\mathbf{2}}{\mathrm{RMe_2SiOH}}$$

Entry	Silylmethanols	Silanols	Yield[a]/%
1	 **1a**	 **2a**	82
2	 **1b**	 **2b**	82
3	 **1c**	 **2c**	88
4	 **1d**	 **2d**	74
5	 **1e**	 **2e**	79
6	 **1f**	 **2f**	84
7	 **1g**	 **2g**	99
8	 **1h**	 **2h**	74
9	 **1i**	 **2i**	27[b]

[a]Isolated yield after silica-gel column chromatography. [b]Multiple spots on TLC.

A plausible mechanism for the silylmethanol–silanol conversion is as follows (Scheme 1). Initially, silylmethanol is normally oxidized to formylsilane.[10] Then, formylsilane is attacked by the hypochlorite ion; this results in a Brook-type rearrangement[11] and elimination of the chlorine atom to afford the formyloxysilane. It is well known that carbonyl groups adjacent to silicon atoms are highly reactive.[12] Finally, hydrolysis of the formyl group affords silanol.

In conclusion, we have developed a novel method for the preparation of silanols. This can be carried out under mild conditions and tolerates a wide range of functional groups.

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