

Highly Selective and Practical Hydrolytic Oxidation of Organosilanes to Silanols Catalyzed by a Ruthenium Complex

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Organosilicon compounds are of paramount importance as versatile building blocks,¹ among which silanols have been prominently utilized in industry for the production of silicon-based polymeric materials² as well as in organic synthesis as valuable equivalents to various functional groups.³ Especially noteworthy is that organosilanols have been recently recognized as an efficient organic donor in metal-catalyzed cross-coupling reactions.⁴ Although the wide utility of silanols requires efficient preparative procedures for the compounds from readily available precursors, only a limited number of methods are available to date, which include hydrolysis of chlorosilanes,^{5a} oxidation of organosilanes with stoichiometric amounts of oxidants,^{5b} or treatment of siloxanes with alkali reagents.^{5c–d} A more promising procedure is the catalytic insertion of the oxygen atom into the Si–H bond of organosilanes, which has been carried out by some metals.⁶ This protocol, however, is rather limited in many cases due to the fact that it normally produces a mixture of the silanol and its undesirable dimer; disiloxane and a ratio of two compounds is capriciously varied especially in the reaction of sterically unencumbered silanes. Moreover, the oxygenation of silanes possessing some functional groups occasionally leads to undesired side products.⁷ During the studies on organic transformations by virtue of the activation of organosilanes,⁸ we have discovered a *highly selective and practical* hydrolytic and catalytic oxidation method of a variety of organosilanes to the corresponding silanols, which is described in this communication.

With the use of water as an oxygen source for practical reasons, oxidation of dimethylphenylsilane was examined in the presence of transition-metal catalysts (Table 1). The sterically exposed silane was chosen as a model substrate because its conversion to the corresponding silanol is highly sensitive to the reaction conditions, and condensation to disiloxane is a serious drawback frequently encountered in most previously reported procedures.^{5,6} Among the ruthenium or rhodium complexes tested, catalysts of

Table 1. Hydrolytic Oxidation of Dimethylphenylsilane Using Various Catalysts^a

entry	catalyst (2 mol %)	H ₂ O (equiv)	under	conv ^b (%)	silanol/disiloxane ^c
1	—	10	air	<1	
2	RuCl ₃ –H ₂ O	2	air	22	2/98
3	RuCl ₂ (PPh ₃) ₃	2	air	42	42/58
4	Ru(cod)Cl ₂	2	air	12	<1/99
5	Ru ₃ (CO) ₁₂	2	air	13	<1/99
6	RhCl(PPh ₃) ₃	2	air	49	77/23
7	RuH ₂ (PPh ₃) ₄	2	air	44	1/99
8	[RuCl ₂ (benzene)] ₂	2	air	98	98/2
9	[RuCl ₂ (<i>p</i> -cymene)] ₂	2	air	>99	>98/2
10 ^d	[RuCl ₂ (<i>p</i> -cymene)] ₂	2	O ₂	>99	>99/1
11 ^e	[RuCl ₂ (<i>p</i> -cymene)] ₂	2	air	98	89/11

^a All reactions were carried out in 0.2 M (CH₃CN) to the silane. ^b Conversion was determined by ¹H NMR spectroscopy, error ±5% of the stated values. ^c Ratios were measured by the integration of ¹H NMR spectroscopy, error ±3% of the stated values. ^d Performed under O₂ atmosphere using an oxygen balloon. ^e THF was used as the solvent.

higher reactivity exhibited, in general, higher preference for the formation of silanol over its dimer. Especially, a dimeric ruthenium catalyst of the type [RuCl₂(arene)]₂ provided the best selectivity as well as the highest reactivity. For example, with the cymene complex, [RuCl₂(*p*-cymene)]₂⁹ (**1**, 2 mol %), the oxidation was completed within 10 min at room temperature with the use of water (2 equiv),¹⁰ in which selectivity for silanol versus disiloxane was extremely high (91/1, entry 9 where denoted as >98/2). The selectivity was further improved (200/1) when the reaction was carried out under an oxygen atmosphere (1 atm).¹¹ CH₃CN was the solvent of choice although other aprotic polar ones such as DMF, DMSO, or THF exhibited comparable reaction rates, in which, however, selectivity for the formation of silanol was lower than that in acetonitrile.

Good yields of organosilanols could be obtained across a wide range of silanes using the established catalyst system (Table 2).¹² Sterically exposed silanes were smoothly oxidized to silanols in excellent yields under mild conditions (condition A: 2 mol % of **1**, 2 equiv of water, room temperature). Selectivity for the formation of silanol versus disiloxane was remarkably high (>98:2) even for the unhindered silanes, and it was not sensitive to the type of substituents on silicon. Geminal dioxygenation of Ph₂SiH₂ could also be efficiently performed to afford diphenylsilanediol (entry 4). However, the reactions were retarded by steric congestion around silicon, and in these cases higher temperatures were necessary to go to completion (condition B: 3 mol % of **1**, 5 equiv of water, 80 °C). It should be mentioned, however, that selectivities were maintained to the same degree regardless of the reaction conditions employed (e.g., compare entries 1 and 2 in Table 2).

With regard to the potential utility of silanols in synthetic chemistry, silanols possessing alkynyl or alkenyl groups are compounds of high interest because they can eventually transfer the unsaturated moiety to other organic acceptors.⁴ Therefore, we turned our attention to the preparation and oxidation of silanes

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(10) Without water, less than 5% conversion was observed under the reaction conditions.

(11) Although the exact role of oxygen is not known at this stage, we found that the reaction rates were also moderately increased under the oxygen atmosphere especially in cases of slow reacting substrates.

(12) Typical procedure: To a solution of dimethylphenylsilane (273 mg, 2.0 mmol) in acetonitrile (6 mL) was added [RuCl₂(*p*-cymene)]₂ (25 mg, 0.04 mmol) and deionized water (72 mg). The reaction mixture was stirred under air for 10 min at room temperature, within which complete conversion was observed. Evaporation of solvent and chromatography on silica gel (hexane/ethyl acetate = 1/30) afforded dimethylphenylsilanol (289 mg, 95%).

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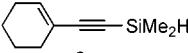
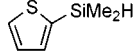
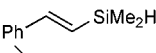
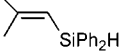
(5) (a) Rochow, E. G.; Gilliam, W. F. *J. Am. Chem. Soc.* **1941**, 63, 798. (b) Adam, W.; Mello, R.; Curci, R. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 890. (c) Sieburth, S. M.; Mu, W. *J. Org. Chem.* **1993**, 58, 7584. (d) Hirabayashi, K.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1997**, 38, 461.

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(7) For example, see: Cavicchioli, M.; Montanari, V.; Resnati, G. *Tetrahedron Lett.* **1994**, 35, 6329.

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Table 2. Oxidation of Organosilanes by $[\text{RuCl}_2(p\text{-cymene})]_2$ (**1**)/ H_2O^a

$\text{R}^1\text{R}^2\text{R}^3\text{SiH} + 1 + \text{H}_2\text{O}$		$\xrightarrow[\text{CH}_3\text{CN}]{\text{air}}$		$\text{R}^1\text{R}^2\text{R}^3\text{SiOH}$
entry	silane	conditions ^b (time)	silanol/ disiloxane ^c	yield ^d
1	PhMe_2SiH	A (10 min)	>98:2	95
2	PhMe_2SiH	B (5 min)	>98:2	89
3	Ph_2MeSiH	A (10 min)	>99:1	97
4 ^e	Ph_2SiH_2	A (10 min)	>99:1	86 ^f
5	Et_3SiH	A (10 min)	>99:1	95
6	$\text{CH}_2(\text{CH}_2)_{17}\text{SiMe}_2\text{H}$	A (3 h)	>99:1	86
7	Ph_3SiH	B (30 min)	>99:1	98
8	$(i\text{-Bu})_3\text{SiH}$	B (4 h)	>99:1	85
9	$\text{Ph}-\text{C}\equiv\text{C}-\text{SiMe}_2\text{H}$	A (10 min)	>99:1	84
10	$\text{Ph}-\text{C}\equiv\text{C}-\text{Si}(i\text{-Pr})_2\text{H}$	B (2 h)	>99:1	72
11	$\text{TMS}-\text{C}\equiv\text{C}-\text{SiMe}_2\text{H}$	A (10 min)	>99:1	92
12	$n\text{-Bu}-\text{C}\equiv\text{C}-\text{SiMe}_2\text{H}$	A (10 min)	>99:1	98
13	$\text{Cl}(\text{CH}_2)_3-\text{C}\equiv\text{C}-\text{SiMe}_2\text{H}$	A (10 min)	>99:1	98
14		A (10 min)	>99:1	98
15		A (10 min)	>99:1	93
16		A (10 min)	98:2	82
17		B (30 min)	>99:1	88
18	$(+/-)\text{-Me}(\alpha\text{-Np})\text{PhSiH}$	B (30 min)	>99:1	98
19 ^g	$(+)\text{-Me}(\alpha\text{-Np})\text{PhSiH}$	B (30 min)	>99:1	97

^a All reactions were carried out in 2.0 mmol scale (0.33 M). ^b Condition A: **1** (2 mol %), H_2O (2 equiv), 25 °C. Condition B: **1** (3 mol %), H_2O (5 equiv), 80 °C. ^c Ratios were determined by ^1H NMR spectroscopy of the crude reaction mixture, error $\pm 3\%$ of the stated values. ^d Refer to isolated yields after chromatography. ^e 4 equiv of water was used in this case. ^f Yield refers to diphenylsilanediol. ^g The optical purity of silane was 76% ee and that of the isolated silanol was 56% ee with inverted configuration.

having alkynyl- or alkenyl groups on silicon.¹³ As demonstrated in Table 2 (entries 9–17), those silanes were oxidized almost exclusively to the corresponding silanols in high yields. Various additional functional groups (e.g., another silicon, halide, conjugated olefin, or sulfur) could also be present on the silanes without affecting the efficiency in the reactions of those substrates. It should be mentioned that oxidation of the alkynyl- or alkenyl-silanes has been problematic in most previous studies due to the

(13) Alkenyl- and alkynylsilanes were readily prepared in good yields by the reaction of a chlorodialkylsilane with lithiated alkenes and alkynes, respectively (for details, see the Supporting Information).

simultaneous oxidation of the unsaturated groups.⁷ Therefore, the present protocol should serve as one of the most selective and mild procedures for the preparation of the functionalized silanols.

With the present catalyst system, oxidation of an optically active silane proceeded with *inversion* of configuration at the silicon center. For example, subjecting (+)-methyl-(α -naphthyl)-phenylsilane¹⁴ to reaction conditions B afforded in high yield the inverted silanol, (–)-(α -Np)PhMeSiOH.¹⁵ For the stereoselective oxidation of optically active silanes, retention of configuration has been observed by the use of stoichiometric oxidants such as peracids, peroxides, or oxiranes.^{6c,d,16} However, to the best of our knowledge, no example of *homogeneous* catalysis has been reported to date to achieve the conversion with inverted configuration.¹⁷

To establish the applicability of the present protocol to larger scale processes, a reaction of 0.1 mol scale of dimethylphenylsilane (13.6 g) was undertaken with water (2.0 equiv) and 0.2 mol % of the catalyst (**1**, 122 mg) in CH_3CN (0.5 M). The oxidation was complete within 5 min at room temperature, and the corresponding silanol was isolated in high yield (13.9 g, 91%). A plausible mechanistic pathway is one in which the ruthenium metal activates a silane to give a silylmetal hydride intermediate, which is subsequently attacked by a nucleophile (water, in this case) from the backside.¹⁸ A peak of the putative ruthenium hydride on ^1H NMR spectroscopy¹⁹ and the observed inversion of silicon configuration during the reaction would be strong evidence for this proposal.

Our results amply demonstrate that with an oxidizing system of $[\text{RuCl}_2(p\text{-cymene})]_2/\text{H}_2\text{O}$, a wide range of organosilanols could be obtained with remarkably high selectivities and in excellent yields from readily available silanes, and that the reaction conditions are mild enough to be applicable to large-scale conversions.

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Supporting Information Available: Spectral data for all new silanes and silanols (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) The optically active silane ($[\alpha]_{\text{D}}^{25}$ 26.5 (*c* 2.1, pentane): ee 76%) was prepared according to the reported method: Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271. Reference 6d describes a modified procedure.

(15) Optical purity of the silanol (ee 56%) was doubly determined through ^1H NMR analysis with $\text{Eu}(\text{hfc})_3$ and by optical rotation: $[\alpha]_{\text{D}}^{25}$ –11.2 (*c* 7.0, ether) [–20.0 (*c* 7.0, ether),^{5b} –20.5 (*c* 6.7, ether)^{12b}]. The optical purity became, interestingly, slightly higher (ee 67%) when condition A was employed.

(16) Sommer, L. H.; Ulland, L. A.; Parker, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3469.

(17) For a previous example, in which inversion of configuration was observed by *heterogeneous* catalysis, see: Sommer, L. H.; Lyons, J. E. *J. Am. Chem. Soc.* **1969**, *91*, 7061.

(18) Although the metal catalyst is different, a similar pathway was considered by Sommer et al. in ref 17.

(19) A peak at –10 ppm (CDCl_3) was observed on ^1H NMR spectroscopy upon mixing triphenylsilane with a stoichiometric amount of **1**, which is in the range of reported values of the ruthenium hydride: Ayllon, J. A.; Sayers, S. F.; Sabo-Etienne, S.; Donnadiou, B.; Chaudret, B. *Organometallics* **1999**, *18*, 3981.