JOC Note

Highly Efficient Iridium-Catalyzed Oxidation of Organosilanes to Silanols

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Received November 9, 2003

Abstract: Hydrolytic oxidation of organosilanes to the corresponding silanols can be performed highly efficiently with a catalyst system of $[IrCl(C_8H_{12})]_2$ under essentially neutral and mild conditions, and various types of silanols are produced in good to excellent yields.

Development of concise methods for the preparation of silanols is highly valuable in the field of synthetic organic chemistry[1] because organosilanols can be utilized both in organic synthesis as versatile building blocks and in industry for the production of silicon-based polymeric materials.[2] In addition, organosilanols have been recently used as a nucleophilic coupling partner in Pd-catalyzed cross-coupling reactions.[3] A variety of preparative procedures of silanols have been developed, including hydrolysis of chlorosilanes,[4] oxidation of organosilanes with stoichiometric amounts of oxidants,[5] and treatment of siloxanes with alkali metal reagents.[6] However, most known methods have a limited scope because silanols are sensitive to dimerization in the presence of even trace amounts of acid or base which are normally found in the reported procedures. Recently, catalytic oxidation of the Si−H bond of organosilanes has been studied extensively with Ni, Pd, Cr, Rh, Re, and Cu complexes.[7] However, these protocols exhibit a rather limited scope to certain substrate types and they produce disiloxanes in high amounts in many cases. Despite the recent progress, there is still a strong need for a highly efficient synthetic method for the conversion of readily available organosilanes to silanols. One of the authors has recently reported a highly selective and practical ruthenium-catalyzed hydrolytic oxidation of organosilanes to the corresponding silanols under relatively mild conditions.[8] To continue our studies on the development of new metal-catalyzed reactions using organosilanes,[9] we reveal herein an additional catalytic oxidation protocol of organosilanes to the corresponding silanols with excellent selectivity and efficiency under mild conditions.

The catalytic activity of several transition metals was examined for the conversion of triethylsilane to triethylsilanol with the use of water as an oxygen source for practical reasons. The sterically exposed silane was chosen as a model compound because its oxidation to the corresponding silanol is highly sensitive to the reaction conditions, and condensation to disiloxane is a serious drawback frequently encountered in most reported procedures.[4−6,10] *Of the catalytic systems screened, the best result was obtained with 1 mol % $[IrCl(C_8H_{12})]_2$*[11] *in the presence of 2 equiv of H_2O at room temperature,* under which triethylsilanol was isolated in 80% yield. *There was no disiloxane formed from the reaction.* Other iridium complexes such as $IrCl(CO)(PPh_3)_2$ and $[Ir(C_8H_{12})_2]^+BF_4^-$ produced triethylsilanol in low yield. CH_3CN was the solvent of choice among several reaction media screened. Triphenylsilane was oxidized to triphenylsilanol using $[IrCl(C_8H_{12})]_2$ and $[RhCl_2(p\text{-cymene})]_2$[8] to compare the reactivities of these catalysts. Although triphenylsilanol was obtained in 10% yield with 1 mol % $[RhCl_2(p\text{-cymene})]_2$ in CH_3CN at 25 °C for 24 h, the corresponding silanol was produced in 83% yield with 1 mol % $[IrCl(C_8H_{12})]_2$ in CH_3CN at 25 °C for 2 h. Therefore, $[IrCl(C_8H_{12})]_2$ is a much more reactive catalyst than $[RhCl_2(p\text{-cymene})]_2$ toward oxidation of silanes.

To demonstrate the efficiency and scope of the present method, we applied the Ir-catalytic system to a variety of organosilanes. Organosilanols were obtained in good to excellent yields across a variety of organosilanes under the optimum conditions (Table 1). Sterically exposed silanes were smoothly oxidized to silanols in high yields under mild conditions. Selectivity for the formation of silanol versus disiloxane was excellent even for the

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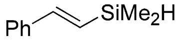
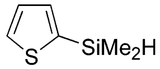
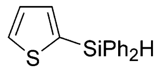
10.1021/jo035647r CCC: $27.50

TABLE 1. Oxidation of Organosilanes to Silanols by $[IrCl(C_8H_{12})]_2/H_2O$

$$R_1R_2R_3SiH \;+\; H_2O \xrightarrow[CH_3CN,\ \textbf{air},\ \textbf{r.t.}]{1\ mol\%\ [IrCl(C_8H_{12})]_2} R_1R_2R_3SiOH$$

entry	organosilane	time(h)	isolated yield(%)[a]
1	Et_3SiH	1	80
2	$(\textit{iso}\text{-}Bu)_3SiH$	2	92[b]
3	$CH_3(CH_2)_{17}SiMe_2H$	3	88
4	$PhMe_2SiH$	1	85
5	Ph_2MeSiH	1	83
6	Ph_3SiH	2	83
		24	10[c]
7	Ph_2SiH_2	0.5	82[d]
8	4-MeO-$PhSiMe_2H$	0.5	87
9	*n*-Bu-$PhSiMe_2H$	0.5	85
10	4-Me-$PhCH_2SiMe_2H$	0.5	82
11		0.5	42
12	$Cl(CH_2)_3{-}C{\equiv}C{-}SiMe_2H$	0.5	22
13	$Ph{-}C{\equiv}C{-}Si(\textit{iso}\text{-}Pr)_2H$	12	96
14		0.5	84
15		0.5	88
16		0.5	83
17	(+/-)-Me(α-Np)PhSiH	2	99
18	(+)-Me(α-Np)PhSiH	2	99

[a] Reaction performed in the presence of 1 mol % $[IrCl(C_8H_{12})]_2$ and 2.0 equiv of H_2O in CH_3CN at 25 °C, unless otherwise noted. [b] Conditions: 3 mol % $[IrCl(C_8H_{12})]_2$ and 5.0 equiv of H_2O in CH_3CN at 80 °C. [c] Conditions: 1 mol % $[RuCl_2(p\text{-cymene})]_2$ and 2.0 equiv of H_2O in CH_3CN at 25 °C.[8] [d] Conditions: 3 mol % $[IrCl(C_8H_{12})]_2$ and 5.0 equiv of H_2O in CH_3CN at 25 °C.

unhindered silanes, and it was observed that the ratio was not sensitive to the type of substituents on the silicon. Silanes having aliphatic substituents on the silicon proceeded smoothly to give silanols without contamination of disiloxane (entries 1−3). Geminal dioxygenation of Ph_2SiH_2 could also be efficiently performed to give diphenylsilanediol in 82% yield under the same conditions (entry 7). Electronic variation on the aromatic substituents did not change the efficiency and selectivity (entries 8 and 9). In the cases possessing a thienyl or quinolinyl group as a substituent on the silicon, the desired silanols were also produced in good yields (entries 14−16). With regard to the potential utility of silanols in synthetic chemistry, silanols having alkenyl or alkynyl groups are very important adducts because they can eventually transfer the unsaturated moiety to other organic acceptors by metal catalysts.[3] Therefore, we turned our attention to the oxidation of silanes possessing alkenyl or alkynyl groups.[12] In the case of silanes having a triple bond, the corresponding silanol was produced in only 22% yield along with several side products mainly due to the oxidation of the unsaturated groups (entry 12). In contast, sterically crowded alkynylsilanes were converted to silanols in much higher yields (entry 13). In the case of sterically hindered organosilanes (entries 17 and 18), $[IrCl(C_8H_{12})]_2$ catalyst yielded the corresponding silanols essentially in quantitative yields at room temperature. It is highly significant to consider the previous experimental results that the ruthenium catalyst sytem, $[RuCl_2(p\text{-cymene})]_2$, afforded the same silanol with comparable yields only at temperatures above 80 °C under otherwise identical conditions.[8] This demonstrates that the catalytic activity of $[IrCl(C_8H_{12})]_2$ is noticeably higher for the hydrolytic oxidation of organosilanes than that of the ruthenium counterpart, $[RuCl_2(p\text{-cymene})]_2$. For the oxidation of an optically active silane, almost a complete racemization was observed with the present catalyst system. For example, treatment of (+)-methyl(α-naphthyl)phenylsilane (76% ee)[10d,13] with the iridium catalyst gave the corresponding silanol with <5% ee, albeit in a quantitative chemical yield under the optimized conditions. To the best of our knowledge, no example of homogeneous catalysis has been reported to date to achieve the conversion with racemization.[10c,14]

Although the mechanism of the oxidation of organosilanes to silanols in the presence of $[IrCl(C_8H_{12})]_2$

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[12] Alkenyl- and alkynylsilanes were readily prepared in good yields by the reaction of a chlorodialkylsilane with lithiated alkenes and alkynes, respectively (for details, see ref 8).

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catalyst is not definitely declared at the present stage, we assume that the Ir metal activates the Si−H bond to give a silylmetal hydride intermediate[8,9b] because a peak at −8.51 ppm (CD_3CN) was observed by ^1H NMR spectroscopy upon mixing triethylsilane with a stoichiometric amount of $[IrCl(C_8H_{12})]_2$. The elucidation of the detailed racemization mechanism for the oxidation of an optically active silane must await further study.

In conclusion, we have demonstrated in this communication that catalytic conversion of organosilanes to silanols can be performed highly efficiently with a catalyst system of $[IrCl(C_8H_{12})]_2$ under *essentially neutral and mild conditions (at room temperature)*, and various types of silanols are produced in good to excellent yields. Importantly, it is worth noting that the Ir(I) catalyst is a commercially available, air-stable, and easily handled complex. In addition, the present oxidation method was performed with the use of water as an oxygen source suitable for a highly atom-economical process.

Experimental Section

Typical Experimental Procedure. To a solution of triphenylsilane (260 mg, 1.0 mmol) in acetonitrile (3 mL) was added $[IrCl(C_8H_{12})]_2$ (7 mg, 0.01 mmol) and deionized water (36 mg, 2.0 mmol). The reaction mixture was stirred under air for 2 h at room temperature. Evaporation of solvent and chromatography on silica gel (hexane/ethyl acetate, 10/1) gave triphenylsilanol (230 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.47 (m, 6H), 7.35−7.20 (m, 9H), 2.79 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.9, 133.3, 129.6, 127.9. IR (film): 3432 (br), 2096, 1638, 1265 cm^{-1}. HRMS (EI) for $C_{18}H_{16}OSi$: calcd, 276.0970; found, 276.0964.

Acknowledgment. This work was supported by Grant No. R02-2003-000-10023-0 of the Basic Research Program of the Korea Science & Engineering Foundation and the CMDS at KAIST.

Supporting Information Available: General section and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035647R