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Communication

Diorganotelluride-Catalyzed Oxidation of Silanes to Silanols under Atmospheric Oxygen

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Diorganotellurides efficiently catalyze the aerobic oxidation of organosilanes under photosensitized conditions to afford the corresponding silanols in excellent yield.

Organosilanols have found widespread use in organic synthesis, particularly in cross-coupling reactions,[1] and in industry as synthons for silicon-based polymeric materials.[2] In general, organosilanols are prepared by hydrolysis of the corresponding chlorosilanes; however, strict pH control is required to prevent the well-known self-condensation to produce undesirable disiloxanes.[3] An alternative approach involves the oxyfunctionalization of Si−H bonds using stoichiometric oxidants such as $KMnO_4$,[4] OsO_4,[5] and dimethyldioxirane.[6] From both the synthetic and environmental viewpoints, it would be preferable to perform the above transformations under catalytic conditions. In this context, several metal-catalyzed systems have been developed for the oxidation of silanes to silanols.[7] Of these, particularly promising are the methods based on rhenium,[8] ruthenium,[9] iridium,[10] and silver[11] catalysis, which generate high chemical yields and selectivities of silanols versus disiloxanes. A majority of the catalytic system employs water or hydrogen peroxide as an oxygen source; however, molecular oxygen is seldom used in these reactions.[12]

We recently reported that the aerobic oxidation of diaryl tellurides under photosensitized conditions produced the corresponding telluroxides and that bulky telluroxides efficiently oxidized benzylic and allylic alcohols, phosphines, and quinones.[13a] Needless to say, it would be more attractive to realize diorganotelluride catalysis by employing molecular oxygen as a terminal oxidant. Although such catalytic oxidation of alcohols has not been achieved yet, we previously reported the first aerobic oxidation of phosphite esters catalyzed by diorganotellurides.[13b] As part of our recent study on the chemistry of organotellurium compounds,[13] we here describe the diorganotelluride-catalyzed oxidation of organosilanes to silanols using molecular oxygen.

We began our investigation with diphenylmethylsilane as a substrate to optimize the reaction conditions. As shown in Table 1, a pyridine solution of silane (0.1 M), 10 mol % bis(2,4,6-trimethylphenyl) telluride (Mes$_2$Te), and hematoporphyrin (10^{-4} M) in an open flask was stirred vigorously and irradiated with a 500 W halogen lamp for 4 h. ^{1}H NMR analysis of the crude product revealed the quantitative formation of diphenylmethylsilanol and the absence of the corresponding disiloxane (entry 1). We were unable to

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(1) (a) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*; Meijere, de A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. *1*, Chapter 4. (b) Hirabayashi, K.; Nishihara, Y.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 7893–7896. (c) Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Org. Lett.* **1999**, *1*, 299–301. (d) Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565–568.

(2) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147–262.

(3) (a) Rochow, E. G.; Gilliam, W. F. *J. Am. Chem. Soc.* **1941**, *63*, 798–800. (b) Sauer, R. O. *J. Am. Chem. Soc.* **1944**, *66*, 1707–1709.

(4) Lickiss, P. D.; Lucas, R. *J. Organomet. Chem.* **1995**, *521*, 229–234.

(5) Valliant-Saunders, K.; Gunn, E.; Shelton, G. R.; Hrovat, D. A.; Borden, W. T.; Mayer, J. M. *Inorg. Chem.* **2007**, *46*, 5212–5219.

(6) Adam, W.; Mello, R.; Curci, R. *Angew. Chem., Int. Ed.* **1990**, *29*, 890–891.

(7) (a) Adam, W.; Garcia, H.; Mitchell, C. M.; Saha-Möller, C. R.; Weichold, O. *Chem. Commun.* **1998**, 2609–2610. (b) Schubert, U.; Lorenz, C. *Inorg. Chem.* **1997**, *36*, 1258–1259. (c) Sommer, L. H.; Lyons, J. E. *J. Am. Chem. Soc.* **1969**, *91*, 7061–7067.

(8) (a) Adam, W.; Mitchell, C. M.; Saha-Möller, C. R.; Weichold, O. *J. Am. Chem. Soc.* **1999**, *121*, 2097–2103. (b) Adam, W.; Saha-Möller, C. R.; Weichold, O. *J. Org. Chem.* **2000**, *65*, 2897–2899. (c) Tan, H.; Yoshikawa, A.; Gordon, M. S.; Espenson, J. H. *Organometallics* **1999**, *18*, 4753–4757. (d) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11938–11939. (e) Corbin, R. A.; Ison, E. A.; Abu-Omar, M. M. *Dalton Trans.* **2009**, 2850–2855.

(9) (a) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011–12012. (b) Mori, K.; Tano, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *New J. Chem.* **2002**, *26*, 1536–1538.

(10) Lee, Y.; Seomoon, D.; Kim, S.; Han, H.; Chang, S.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 1741–1743.

(11) Mitsudome, T.; Arita, S.; Mori, H.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 7938–7940.

(12) Minisci, F.; Recupero, F.; Punta, C.; Guidarini, C.; Fontana, F.; Pedulli, G. F. *Synlett* **2002**, 1173–1175.

(13) (a) Oba, M.; Endo, M.; Nishiyama, K.; Ouchi, A.; Ando, W. *Chem. Commun.* **2004**, 1672–1673. (b) Oba, M.; Okada, Y.; Nishiyama, K.; Ando, W. *Org. Lett.* **2009**, *11*, 1879–1881. (c) Oba, M.; Okada, Y.; Nishiyama, K.; Shimada, S.; Ando, W. *Chem. Commun.* **2008**, 5378–5380.

**Table 1.** Diorganotelluride-Catalyzed Oxidation of Ph_2MeSiH Using Atmospheric Oxygen

$$Ph_2MeSiH \xrightarrow[hv,\ sensitizer,\ air,\ 4\ h]{catalyst\ (10\ mol\ \%)} Ph_2MeSiOH$$

entry	catalyst	solvent (sens)[a]	temp (°C)	yield (%)[b]
1	Mes_2Te	pyridine (HP)	50−70	>99
2	Mes_2Te^c	pyridine (HP)	50−70	41
3	Mes_2Te	pyridine (HP)	10−20	>99
4	Mes_2Te	CH_3CN (RB)	50−60	97
5	Mes_2Te	CH_3CN (RB)	10−20	29
6	Mes_2Te	benzene (TPP)	50−70	47
7	Mes_2Te	benzene (TPP)	10−20	28
8	Mes_2Te	CH_2Cl_2 (TPP)	10−20	19
9	An_2Te	pyridine (HP)	50−70	43
10	Ph_2Te	pyridine (HP)	50−70	11

[a] Hematoporphyrin, rose bengal, and tetraphenylporphyrin are abbreviated as HP, RB, and TPP, respectively. [b] Yields were determined by ^{1}H NMR spectroscopy. [c] Catalyst at 1 mol %. Even after 8 h, the yield remained at 55% because of catalyst decomposition.

complete the oxidation by decreasing the catalytic amount to 1 mol % (entry 2). In these reactions, the temperature increased to 50−70 °C during irradiation. An ice bath can be used to maintain the reaction temperature around 10−20 °C (entry 3); however, lower temperatures resulted in diminished chemical yields in some cases (entries 5 and 7). Although acetonitrile served as a good solvent to give silanol in 97% yield (entry 4), the use of benzene and dichloromethane resulted in lower yields (entries 6 and 8). The use of other tellurides, such as bis(4-methoxyphenyl) telluride (An_2Te) and Ph_2Te, as a catalyst failed to afford acceptable yields (entries 9 and 10). The catalyst decomposition may be competitive, owing to the less hindered nature of these tellurides.

The reaction did not proceed without the catalyst, photosensitizer, or light, indicating participation of both the telluride catalyst and singlet oxygen in the catalytic system. Analogous to the catalytic oxidation of phosphite, which we previously reported,[13b] a catalytic cycle is postulated, as shown in Scheme 1. The diaryl telluroxide generated by the singlet-oxygen oxidation of telluride would serve as an oxidant for the silanes. In fact, stoichiometric oxidation of Ph_2MeSiH with isolated Mes_2TeO in pyridine at room temperature for 1 h afforded 95% yield of $Ph_2MeSiOH$ along with the quantitative recovery of Mes_2Te. The stoichiometric oxidation exhibited solvent effects similar to those observed in the catalytic oxidation, even though the extent was not as large. We assume that stabilization of a polar intermediate, such as a silicate (vide infra), by polar solvents is a driving force for the efficient formation of silanols. At present, however, we cannot explain why pyridine is the best solvent in this reaction. Detailed mechanistic investigations are now underway.

The optimized conditions of entry 1 in Table 1 were applied to the reaction of various triorganosilanes, the results of which are listed in Table 2. In all cases, triorganosilanols were obtained in excellent yields, and only trace amounts of the corresponding disiloxanes were detected in the reaction mixture. For example, sterically encumbered triphenylsilane afforded triphenylsilanol in a quantitative yield (entry 1). Monoarylsilanes bearing either electron-withdrawing or electron-donating groups (entries 3−6), as well as a heterocyclic silane (entry 7), underwent catalytic oxidation, affording the

Scheme 1. Proposed Catalytic Cycle for Ar_2Te-Catalyzed Oxidation of Triorganosilanes
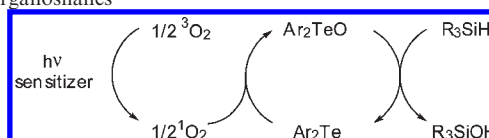
Table 2. Mes_2Te-Catalyzed Oxidation of Triorganosilanes (R_3SiH) Using Molecular Oxygen

$$R_3SiH \xrightarrow[pyridine,\ hv,\ air,\ 50-70\ °C]{Mes_2Te\ (10\ mol\ \%),\ HP} R_3SiOH + (R_3Si)_2O$$

			yield (%)[a]	
entry	R_3SiH	time (h)	R_3SiOH	$(R_3Si)_2O$
1	Ph_3SiH	4	>99 (96)	<1
2	Ph_2MeSiH	4	>99 (93)	<1
3	$PhMe_2SiH$	4	>87 (74)	<1
4	$(4\text{-}MeOC_6H_4)Me_2SiH$	6	>94 (89)	<1
5	$(4\text{-}ClC_6H_4)Me_2SiH$	4	>94 (82)	<1
6	$(4\text{-}CF_3C_6H_4)Me_2SiH$	4	>95 (87)	<1
7	$(2\text{-}thienyl)Me_2SiH$	4	>91 (83)	<1
8	$(1\text{-}dodecyl)Me_2SiH$	10	>92	<1
9[b]	$(1\text{-}dodecyl)Me_2SiH$	4	>99 (95)	<1
10[b,c]	Et_3SiH	4	>99	<1

[a] Yields were determined by ^{1}H NMR spectroscopy, except for entry 10 (GC yield). Isolated yields of silanols are shown in parentheses. [b] In the presence of 20 mol % Mes_2Te. [c] The reaction was performed in a sealed flask to prevent volatilization of triethylsilane under an oxygen atmosphere.

corresponding silanols in excellent yields. For the oxidation of trialkylsilanes, such as 1-dodecyldimethylsilane (entries 8 and 9) and triethylsilane (entry 10), increasing the reaction time or the amount of catalyst was required to obtain satisfactory yields. It appears that the more aryl-substituted or electron-deficient silanes tend to have higher reactivities.

In order to quantify the electronic effects of the substituents at the silicon atom, we examined the linear free-energy relationships (LFERs) between the reaction rates and the substituent constants. A Hammett plot, derived from the relative rates of oxidation conducted with a series of 4-substituted phenyldimethylsilanes, yields a linear correlation (correlation coefficient $R^2 = 0.98$) with σ_p parameters (Figure 1).[14] Figure 1 shows that the more electron-deficient silanes react faster, and the substantial positive slope ($\rho = 2.09$) indicates that a significant negative charge develops on the silicon atom in the transition state of the rate-determining step; this is in good agreement with the proposed mechanism described below.

The present catalyst system could be applied successfully to the stereoselective oxidation of an optically active silane. As shown in Scheme 2, the Mes_2Te-catalyzed aerobic oxidation of (R)-(+)-Me(α-Np)PhSiH (96% ee) under photosensitized conditions afforded (S)-(+)-Me(α-Np)PhSiOH in 79% isolated yield (86% NMR yield) with 89% ee.[15] The

(14) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

(15) The ee values were determined by comparing specific rotations with the literature data. (R)-(+)-Me(α-Np)PhSiH: $[\alpha]^{26}_D$ +32.3 (*c* 3.99, cyclohexane) [lit. $[\alpha]_D$ +33.7 (*c* 4.00, cyclohexane)]. (S)-(+)-Me-(α-Np)PhSiOH: $[\alpha]^{24}_D$ +18.2 (*c* 5.98, Et_2O) [lit. $[\alpha]_D$ +20.5 (*c* 6.66, Et_2O)]. For literature, see: Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271−3276.
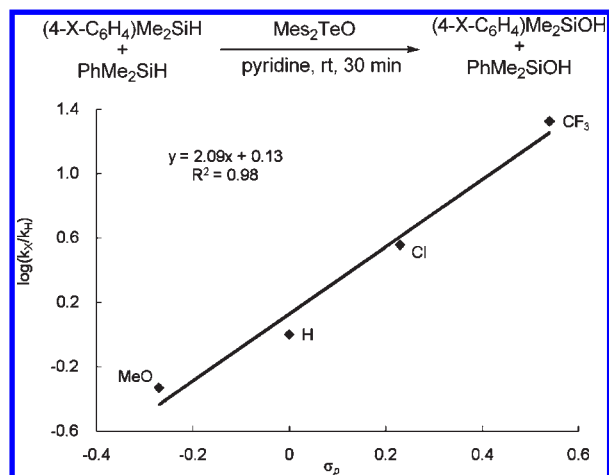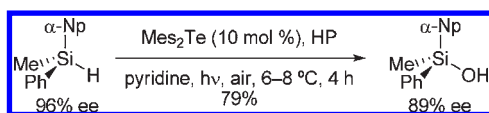
Figure 1. Hammett plot illustrating the electronic effects of 4-substituted phenyldimethylsilanes on the oxidation rate.

Scheme 2. Stereoselective Oxidation of Optically Active Silane


oxidation proceeded with a high degree (93% optical yield) of retention of the configuration at the silicon atom. Although it is well-known that stoichiometric oxidants, such as *m*-CPBA,[16] dimethyldioxirane,[6] and oxaziridines,[17] transform the optically active silane with retention of the configuration, catalytic methods that achieve stereoselective oxidation are rare. Our results are comparable to those reported by Adam and co-workers,[8a] who demonstrated that methyltrioxorhenium efficiently catalyzed the oxidation of the optically active silane with 96% retention. Another example of the catalytic oxidation of the optically active silane involved a ruthenium complex–H_2O system, which yielded the corresponding silanol with 74% inversion.[9a] Later, similar hydrolytic oxidation using an iridium catalyst was reported and shown to result in the formation of a racemic silanol.[10]

A possible reaction mechanism that can account for the stereochemical and kinetic results described above is

Scheme 3. Plausible Reaction Mechanism for the Oxidation of Triorganosilane with Diaryl Telluroxide
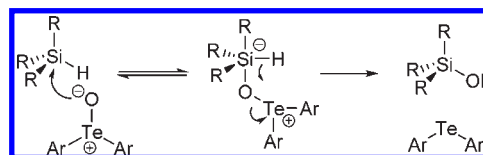
Scheme 4. KIE for the Oxidation of Ph_2MeSiH versus Ph_2MeSiD by Mes_2TeO
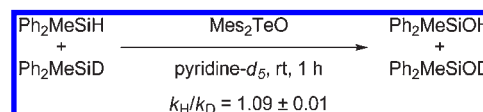
illustrated in Scheme 3. Namely, an attack by the nucleophilic oxygen atom of the telluroxide on the silicon atom, generating a zwitterionic silicate intermediate, is rate-determining. This is followed by a rapid hydrogen shift from the silicon to the oxygen to ensure retention of stereochemistry at the silicon atom, producing a silanol and a telluride.

We also investigated the reaction by studying the kinetic isotope effect (KIE). A 1:1 mixture of Ph_2MeSiH and Ph_2MeSiD was treated with Mes_2TeO in pyridine-d_5 at room temperature for 1 h (Scheme 4). ^1H NMR analysis of the reaction mixture exhibited a small KIE ($k_H/k_D = 1.09 \pm 0.01$). The Si–H bond-breaking process was not rate-determining, which is in line with the proposed mechanism.

In conclusion, we have developed a novel approach to the synthesis of triorganosilanols based on the diorganotelluride-catalyzed oxidation of silanes employing atmospheric oxygen as an oxidant. The oxidation proceeds with excellent selectivity in favor of silanols versus disiloxanes. The stereoselective oxidation of an optically active silane is also achieved to produce the corresponding silanol with high retention of the configuration. Studies on LFER and KIE indicate that the attack by telluroxide on silane in producing a silicate intermediate is rate-determining.

Supporting Information Available: Details of experimental procedures and characterization data for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(16) Sommer, L. H.; Arie Ulland, L.; Parker, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3469–3471.

(17) Cavicchioli, M.; Montanari, V.; Resnati, G. *Tetrahedron Lett.* **1994**, *35*, 6329–6330.