Oxidation of 2-Pyridyldimethylsilyl Group to Hydroxyl Group by H_2O_2/KF. Implication of Fluoride Ion Accelerated 2-Pyridyl−Silyl Bond Cleavage

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Introduction

Silicon−carbon bonds are generally quite stable to most of the synthetic reagents and manipulations including oxidants. Therefore, the oxidative cleavage of silicon−carbon bond is one of the challenging topics in silicon chemistry.[1−7] In 1983, Tamao and co-workers have found that the silicon−carbon bonds can be cleaved by hydrogen peroxide to afford the corresponding alcohol (eq 1).[8] This was the first bona fide case of the practical oxidative cleavage of silicon−carbon bonds. The only limitation might be that it requires at least one electron-withdrawing group such as an alkoxy group on silicon. In 1984,

Tamao Oxidation

$$R-SiX_3 \xrightarrow[\text{several conditions}]{30\%\ H_2O_2} R-OH \qquad (1)$$

SiX_3 = $SiMe_2H$, $SiMe_2F$, $SiMe_2Cl$, $SiMeCl_2$, $SiCl_3$, $SiMe_2(NEt_2)$, $SiMe_2(OEt)$, $SiMe(OEt)_2$, $Si(OEt)_3$ etc.

Fleming and co-workers found that the $PhMe_2Si-C$ bond can be cleaved oxidatively in two steps (eq 2).[9] These two

Fleming Oxidation

$$R-SiMe_2Ph \xrightarrow[BF_3\bullet 2AcOH]{HBF_4\bullet OEt_2\ \text{or}} R-SiMe_2X \quad (X = F \text{ or } OAc) \xrightarrow[\text{mCPBA, KF, DMF}]{\text{mCPBA, } Et_3N, Et_2O\ \text{or}} R-OH \qquad (2)$$

landmark achievements have served to galvanize the preexisting interest in the silicon-based reagents in the synthetic community. To date, certain silyl groups have been well recognized as important hydroxyl group surrogates in modern organic synthesis. Listed in Chart 1 are the other representative silyl groups which can be oxidatively converted to hydroxyl group.[10−21]

Recently, we have developed a 2-pyridyldimethylsilyl (2-$PyMe_2Si$) group as a multifunctional phase tag in solution phase synthesis.[22] The 2-$PyMe_2Si$ group makes the phase switching feasible, thereby enabling easy purification of 2-pyridylsilylated compounds by simple acid−base extraction. Phase tagging (introduction of 2-$PyMe_2Si$ group to organic molecules) is easily accomplished by the rhodium(I)-catalyzed hydrosilylation of alkenes. When confronted with the detagging of the phase tag (removal of 2-$PyMe_2Si$ group), we searched for a convenient method for the oxidative cleavage of the 2-$PyMe_2Si-C$ bond. We examined Tamao's procedure for the detagging protocol and found that the 2-$PyMe_2Si$

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Chart 1. Representative Silyl Groups for Oxidation

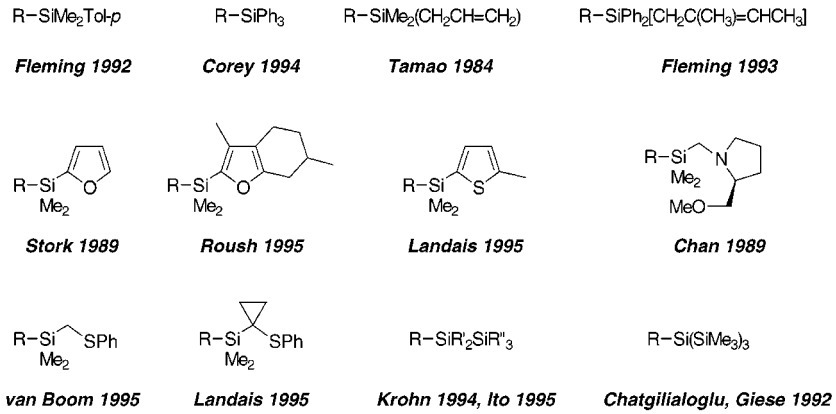
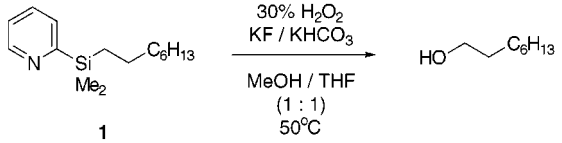


Table 1. H_2O_2 Oxidation of 1 under Several Conditions



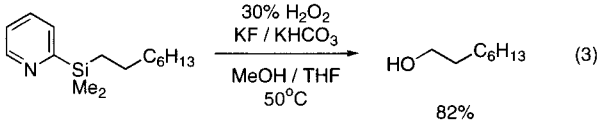
1

entry	H_2O_2 (equiv)	KF (equiv)	$KHCO_3$ (equiv)	yield (%)[a]
1	12	0	1.1	0
2	12	2.0	0	59
3[b]	12	2.0	0	13
4	12	1.6	2.0	61
5	20	2.0	2.0	77
6	30	2.0	2.0	82

[a] Determined by GC analysis. [b] Reaction without MeOH.

2 3

group can be easily converted to a hydroxyl group by hydrogen peroxide in the presence of fluoride ion (eq 3).



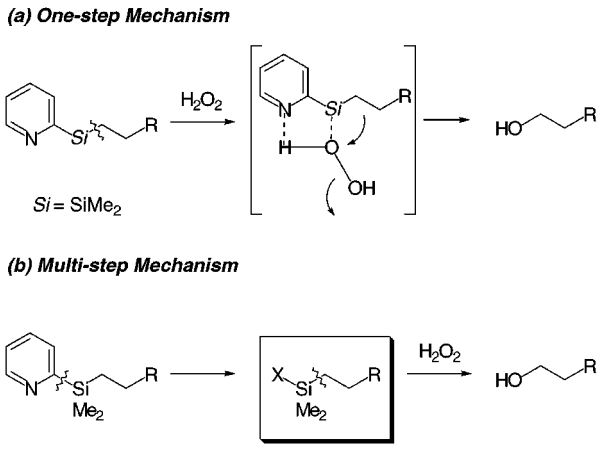
(3)

However, this observation was rather surprising since the oxidation of related $PhMe_2Si$ group has been already known to occur only in Fleming's two-step procedure but not with Tamao's procedure. This prompts us to examine the reaction conditions and mechanism of the cleavage of the 2-$PyMe_2Si$−C bond in detail. In this paper we report the results of this study.

Results and Discussion

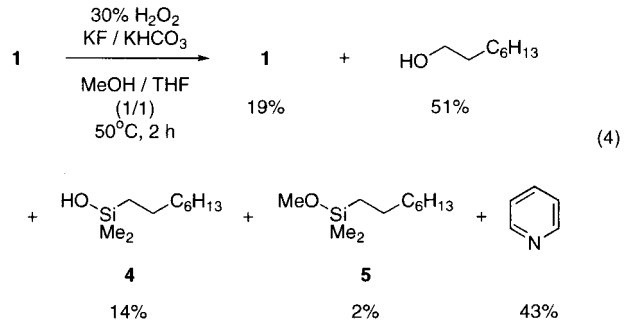
Oxidative Cleavage of the 2-$PyMe_2Si$−C Bond Using Tamao's Procedure. We first chose to follow the lead of Tamao who has reported several reaction conditions for the H_2O_2 oxidation of silicon−carbon bonds. The oxidation of *n*-octyl(2-pyridyl)dimethylsilane (**1**) under several conditions was examined, and the results are depicted in Table 1. Reaction did not proceed at all in the absence of KF (entry 1). When 2.0 equiv of KF was employed, the oxidation proceeded smoothly to afford 1-octanol in 59% yield (entry 2). The absence of methanol had a detrimental effect on yield (entry 3). Increase of the amount of H_2O_2 resulted in higher yields (entries 5 and 6). Finally, the highest yield (82%) was observed when 30 equiv of H_2O_2 was employed in the reaction (entry 6). Interestingly, this H_2O_2 oxidation was found to be characteristic to the 2-pyridyl group since neither *n*-octyl(3-pyridyl)dimethylsilane (**2**) nor *n*-octylphenyldimethylsilane (**3**) gave 1-octanol under the best reaction conditions for **1** (entry 6).

Scheme 1

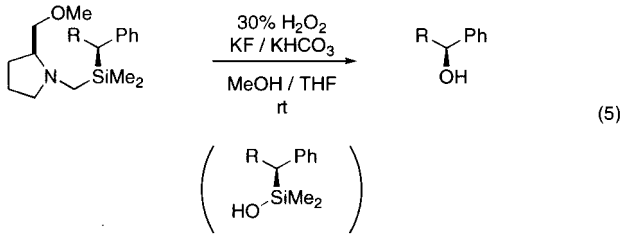


Mechanistic Hypothesis. We were delighted to find that the 2-$PyMe_2Si$−C bond can be oxidatively cleaved to give the corresponding alcohol with the modified Tamao procedure. However, there are several critical questions to be addressed; why is this transformation characteristic to the 2-$PyMe_2Si$ group and how the 2-$PyMe_2Si$−C bond is cleaved. There might be two possibilities for the mechanism of this oxidation. One possibility is that **1** undergoes direct cleavage of the 2-$PyMe_2Si$−C bond (Scheme 1, a). The second possibility is a two-step mechanism involving the initial cleavage of the 2-Py−Si bond (Scheme 1, b).

Quenching the Reaction at the Halfway. We considered that the full analysis of the products at the halfway of the reaction should be instrumental in addressing these issues. Therefore, the oxidation of *n*-octyl-(2-pyridyl)dimethylsilane (**1**) was quenched by the addition of H_2O and Et_2O in 2 h (eq 4). The reaction gave 14% of *n*-octyl(hydroxy)dimethylsilane (**4**), 2% of *n*-octyl-(methoxy)dimethylsilane (**5**), and 43% of pyridine together with 51% of 1-octanol and 19% of unchanged **1**. Identification of hydroxysilane **4** intimates its intermediacy in the oxidation of **1**. Chan reported the Si−C bond



cleavage of the aminomethylsilanes under Tamao's H_2O_2 oxidation conditions (eq 5).[17] Although the mechanism



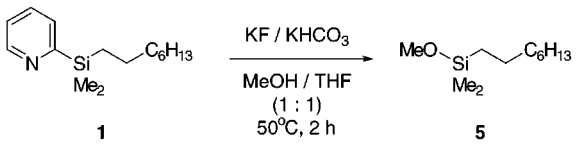
has not been clarified, hydroxysilane was detected at the halfway of the reaction as well.[17a]

Attempt to Convert 2-Pyridylsilane to Hydroxysilane. Encouraged by the detection of **4** at the halfway of the reaction, the feasibility of the direct conversion of 2-pyridylsilane **1** to hydroxysilane **4** has been examined. The reactions were performed with or without KF and $KHCO_3$ in H_2O/THF (1/20) at 50 °C for 2 h. H_2O_2 was omitted from the reactions since hydroxysilanes are already known to undergo H_2O_2 oxidation. However, the reactions did not proceed at all to recover the starting material **1** in quantitative yields.

Attempt to Convert 2-Pyridylsilane to Methoxysilane. Next, we turned our attention to the contaminative production of methoxysilane **5** at the halfway of the reaction (eq 4) and the feasibility of the initial conversion of **1** to **5** has been examined. Again, the reactions were performed in the absence of H_2O_2 since alkoxysilanes are also known to undergo H_2O_2 oxidation. The results were depicted in Table 2. When the reaction was performed in the absence of H_2O_2 but otherwise identical to the optimized conditions in eq 3, **5** was obtained in 72% yield (entry 1). The reaction without $KHCO_3$ also gave **5** in nearly identical yield (74%, entry 3). Decreasing the amount of KF to 1.0 equiv slowed the reaction rate but gave **5** in 81% yield at 100% conversion (entry 4). However, when the reaction was carried out in the absence of KF, only a trace amount of **5** was formed (entry 5). The role of KF has not yet been completely elucidated; however, this addend clearly accelerated the reaction. These observations shown in Table 2 and the failure of the direct conversion of **1** to **4** strongly denote that **5** is the initial intermediate in the oxidation of **1**.

Attempt to Convert Methoxysilane to Hydroxysilane. On the assumption that **4** might form by the hydrolysis of **5** at the halfway of the reaction, we next examined the hydrolysis of **5** in the absence of H_2O_2. The reactions were performed with or without KF and $KHCO_3$ in MeOH/THF/H_2O (1/1/1) at 50 °C for 2 h. When the reactions were carried out in the presence of KF (2.0 equiv) and $KHCO_3$ (2.0 equiv), **5** was hydrolyzed to give

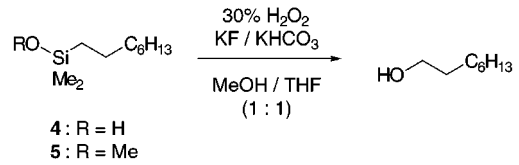
Table 2. Examination of the Conversion of 1 to 5



entry	KF (equiv)	$KHCO_3$ (equiv)	conversion (%)[a]	yield (%)[a]
1	2.0	2.0	100	72
2[b]	2.0	2.0	100	60
3	2.0	0	100	74
4[c]	1.0	2.0	100	81
5	0	2.0	4	4

[a] Determined by GC analysis. [b] Reaction for 20 h at 20 °C. [c] Reaction for 20 h.

Table 3. H_2O_2 Oxidation of 4 and 5[a]



entry	R	temperature (°C)	yield (%)
1	H	20	53
2	H	50	76
3[b]	H	50	11
4	Me	20	58
5	Me	50	68
6[b]	Me	50	31

[a] All reactions were performed with 30% H_2O_2 (30 equiv), KF (2.0 equiv), and $KHCO_3$ (2.0 equiv) in MeOH/THF (1:1) under argon for 8 h. [b] Reaction without KF.

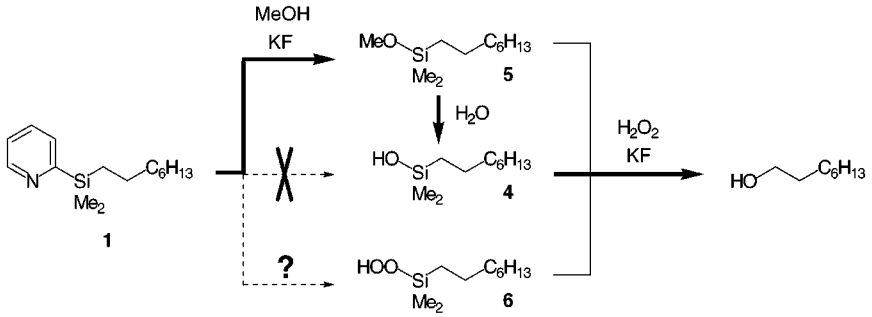
4 in 88% yield (91% conversion). The reaction without $KHCO_3$ gave almost identical yield of **4** (92% yield at 93% conversion). On the other hand, the absence of KF substantially slowed the reaction (50% yield at 50% conversion).

H_2O_2 Oxidation of Hydroxysilane and Methoxysilane. Hydroxysilanes[11b] and alkoxysilanes[8] are already known to undergo H_2O_2 oxidation. To firmly validate that this was also true for our conditions, we next examined the H_2O_2 oxidation of **4** and **5** (Table 3). As we expected, both **4** and **5** underwent H_2O_2 oxidation to give 1-octanol in 76 and 68% yields, respectively. Again, the absence of KF had a detrimental effect in the oxidation (entries 3 and 6).

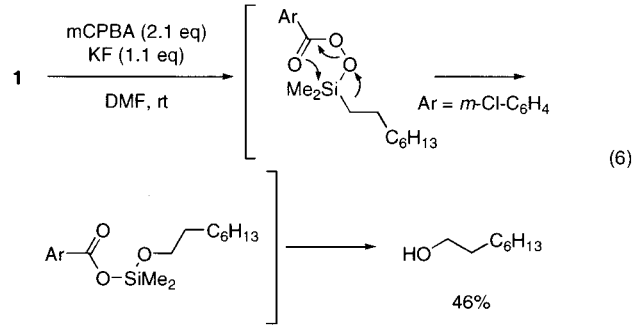
Mechanism of 2-PyMe$_2$Si−C Bond Cleavage. Supported by the experimental results mentioned above, we propose that the H_2O_2 oxidation of **1** proceeds by the mechanism shown in Scheme 2.[23] Initially, 2-pyridylsilane (**1**) reacted with methanol in the presence of fluoride ion to afford methoxysilane (**5**). Under the reaction conditions, this methoxysilane may undergo either hydrolysis to afford hydroxysilane (**4**) or the H_2O_2 oxidation to give 1-octanol as a final product. A mechanism involving the initial formation of perhydroxysilane (**6**) seems to be also possible. This may account for the fact that the best yields through the stepwise reactions are lower than the one-pot reaction yield. Preliminary result on the *m*-CPBA oxidation of **1** in nonalcoholic solvent

(23) Alternatively, one could expect that the oxidation of the pyridyl group first occurs to give the corresponding *N*-oxide, which can then undergo β-elimination to give **4** and 2-hydroxypyridine or 2-methoxypyridine. However, none of these products except **4** were detected in the reaction mixture, which suggests that the mechanism involving *N*-oxide β-elimination is not the case.

Scheme 2

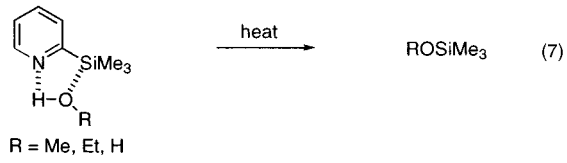


such as DMF also supports the possibility of this reaction pathway, albeit with lower yield (eq 6).



(6)

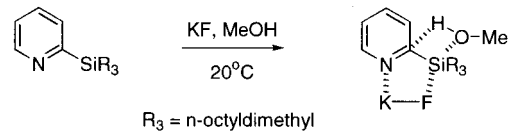
The question which we must consider next is the remarkable effect of 2-pyridyl group and the fluoride ion acceleration on the cleavage of 2-Py−Si bond (**1** to **5**). Webster had proposed in his pioneering work that the solvolysis of 2-pyridyltrimethylsilane by alcohols and water proceeds via cyclic transition state as shown in eq 7.[24] In our case, methanolysis or hydrolysis in the absence



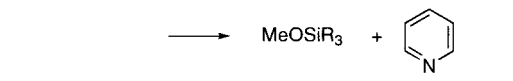
(7)

of fluoride ion was extremely slow presumably because of the steric hindrance around the silicon atom.

A tentative rationalization of our results in the fluoride ion accelerated cleavage of 2-Py−Si bond is given in eq 8. In this intermediate, the potassium ion is coordinated with the nitrogen and the silicon is coordinated with fluoride ion and methanol oxygen. Thus, the reaction occurs only with 2-pyridylsilane but not with the corresponding 3-pyridyl and phenylsilanes. The ab initio molecular orbital calculations of the model compound support the feasibility of the proposed intermediate (eq 9, Figure 1).[25] According to the calculations, 2-PySiH_3 and KF form the stable complex (**7**) where the silicon atom adopt pentacoordination (Figure 1). Complex **7** was found to be −22.9 kcal/mol stable than 2-PySiH_3 and KF at the MP2/LANL2DZ level. Presumably, the resulting pentacoordinated complex is further attacked by MeOH to afford the proposed hexacoordinate complex (eq 8). In the



(8)



(9)

-22.9 kcal/mol
(MP2/LANL2DZ)

hexacoordinate transition state, the 2-pyridyl−silyl bond should be weakened so that it is readily cleaved to result in the formation of methoxysilane and pyridine even at 20 °C.

Conclusion

We have observed the remarkable effect of the 2-pyridyl group on the oxidative cleavage of carbon−silicon bond under Tamao's conditions. Mechanistic studies revealed that the H_2O_2 oxidation of **1** proceeds by the initial cleavage of the 2-Py−Si bond assisted by KF followed by normal Tamao oxidation of the resulting methoxysilane.

Experimental Section

General Methods. Unless otherwise noted, ^1H, ^{13}C, and ^{29}Si NMR spectra were measured at 300, 75, and 60 MHz, respectively. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled under argon from sodium benzophenone ketyl prior to use. Methanol was distilled from $Mg(OMe)_2$.

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(25) The ab initio molecular orbital calculations were carried out at the MP2/LANL2DZ level with geometry optimization using Gaussian 98, Revision A.6.: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

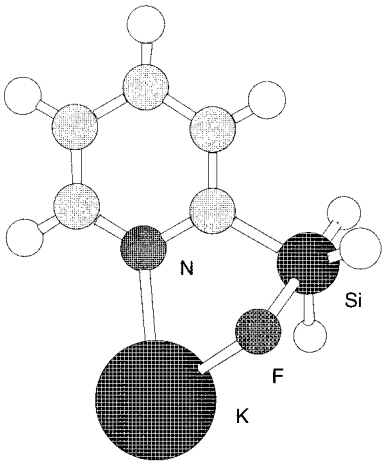

Figure 1. Geometry of **7** (MP2/LANL2DZ).

Dimethyl(2-pyridyl)silane. To a solution of 2-bromopyridine (40.4 g, 255.5 mmol) in Et_2O (80 mL) was added dropwise a *n*-hexane solution of *n*-butyllithium (255 mmol) at −72 °C under argon. The mixture was stirred at −72 °C for an additional 2 h. The resultant solution of 2-pyridyllithium was added to a solution of chlorodimethylsilane (23.2 g, 245.6 mmol) in Et_2O (60 mL) at −72 °C. After stirring at room temperature for 1 h, the mixture was washed with H_2O (4 × 100 mL), and then the organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure and subsequent distillation afforded the title compound in 86% purity as judged by capillary GC. Second distillation afforded the title compound (12.1 g, 36%) as a colorless liquid in a pure form: bp 68−72 °C/20 mmHg. ^{1}H NMR (300 MHz): δ 0.40 (d, J = 3.9 Hz, 6 H), 4.46 (septet, J = 3.9 Hz, 1 H), 7.22 (ddd, J = 7.5, 4.8, 1.2 Hz, 1 H), 7.54 (ddd, J = 7.5, 1.8, 1.2 Hz, 1 H), 7.60 (td, J = 7.5, 1.8 Hz, 1 H), 8.77 (ddd, J = 4.8, 1.8, 1.2 Hz, 1 H); ^{13}C NMR (75 MHz): δ −4.8, 123.1, 129.8, 134.2, 150.4, 165.8; ^{29}Si NMR (60 MHz): δ −19.3 (d, J = 3.6 Hz); IR (neat) 2124, 1576, 1559, 1420, 1248 cm^{-1}; HRMS *m/e* calcd for $C_7H_{11}NSi$: 137.0661, found 137.0658.

Dimethyl(3-pyridyl)silane. By the similar procedure to that used to prepare dimethyl(2-pyridyl)silane, the title compound was obtained from 3-bromopyridine (78%) as a pale yellow liquid: bp (bulb-to-bulb distillation) 120−150 °C/20 mmHg. ^{1}H NMR (300 MHz): δ 0.38 (d, J = 3.9 Hz, 6 H), 4.46 (septet, J = 3.9 Hz, 1 H), 7.30 (dd, J = 7.5, 4.8 Hz, 1 H), 7.85 (dt, J = 7.5, 1.8 Hz, 1 H), 8.60 (dd, J = 4.8, 1.8 Hz, 1 H), 8.71 (t, J = 1.8 Hz, 1 H); ^{13}C NMR (75 MHz): δ −4.3, 123.3, 132.4, 141.7, 150.3, 154.5; ^{29}Si NMR (60 MHz): δ −18.0 (d, J = 3.6 Hz); IR (neat) 2124, 1574, 1557, 1395, 1252 cm^{-1}. Anal. Calcd for $C_7H_{11}NSi$: C, 61.25; H, 8.08; N, 10.20. Found: C, 61.05; H, 8.18; N, 10.00.

Dimethyl(1-octyl)(2-pyridyl)silane (1). To a solution of dimethyl(2-pyridyl)silane (1.10 g, 8.01 mmol) in Et_2O (10 mL) was added dropwise a solution *n*-octyllithium (6.57 mmol, 0.55 M in Et_2O) under argon at −72 °C over 1 h. After stirring at room temperature for 17 h, the mixture was washed with H_2O (3 × 30 mL). The organic phase was additionally extracted with 1 N aq HCl (5 × 30 mL). The aqueous phase was basified to pH 14 by adding NaOH pellet and was extracted with Et_2O (3 × 50 mL). Drying over Na_2SO_4 and removal of the solvents under reduced pressure afforded **1** (1.18 g, 72%) as a colorless oil: ^{1}H NMR (500 MHz): δ 0.30 (s, 6 H), 0.80−0.84 (m, 2 H), 0.86 (t, J = 7.1 Hz, 3 H), 1.20−1.37 (m, 12 H), 7.18 (ddd, J = 7.7, 5.0, 1.5 Hz, 1 H), 7.48 (dt, J = 7.7, 1.5 Hz, 1 H), 7.57 (td, J = 7.7, 1.5 Hz, 1 H), 7.77 (dt, J = 5.0, 1.5 Hz, 1 H); ^{13}C NMR (125 MHz): δ −3.6, 14.1, 14.8, 22.6, 23.7, 29.22, 29.23, 31.9, 33.5, 122.6, 129.0, 133.8, 150.1, 168.0; ^{29}Si NMR (60 MHz): δ −4.4; IR (neat) 1576, 1559, 1417, 1246 cm^{-1}; HRMS *m/e* calcd for $C_{15}H_{27}NSi$: 249.1913, found 249.1911. Anal. Calcd for $C_{15}H_{27}NSi$: C, 72.22; H, 10.91; N, 5.61. Found: C, 72.31; H, 10.63; N, 5.63.

Dimethyl(1-octyl)(3-pyridyl)silane (2). To a solution of dimethyl(3-pyridyl)silane (403 mg, 2.94 mmol) in Et_2O (10 mL) was added dropwise a solution *n*-octyllithium (3.24 mmol, 0.55 M in Et_2O) under argon at −72 °C over 1 h. After stirring at room temperature for 17 h, the mixture was washed with saturated aq $NaHCO_3$ (3 × 5 mL). The organic phase was dried over K_2CO_3 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 as eluents) to give **2** (351 mg, 43%) as a pale yellow oil: ^{1}H NMR (500 MHz): δ 0.27 (s, 6 H), 0.72−0.79 (m, 2 H), 0.86 (t, J = 7.0 Hz, 3 H), 1.19−1.32 (m, 12 H), 7.23 (ddd, J = 7.4, 4.9, 1.0 Hz, 1 H), 7.75 (dt, J = 7.4, 1.9 Hz, 1 H), 8.55 (dd, J = 4.9, 1.9 Hz, 1 H), 8.66 (dd, J = 1.9, 1.0 Hz, 1 H); ^{13}C NMR (125 MHz): δ −3.3, 14.1, 15.4, 22.6, 23.7, 29.17, 29.19, 31.8, 33.5, 123.1, 134.4, 141.2, 149.8, 154.0; ^{29}Si NMR (60 MHz): δ −3.0; IR (neat) 1574, 1559, 1393, 1250 cm^{-1}; HRMS *m/e* calcd for $C_{15}H_{27}NSi$: 249.1913, found 249.1919. Anal. Calcd for $C_{15}H_{27}NSi$: C, 72.22; H, 10.91; N, 5.61. Found: C, 72.12; H, 11.19; N, 5.57.

Typical Procedure for the H_2O_2 Oxidation of 1 (Table 1, entry 6). To a mixture of KF (116 mg, 2.0 mmol) and $KHCO_3$ (200 mg, 2.0 mmol) in MeOH (2.5 mL) and THF (2.5 mL) were added **1** (248 mg, 1.0 mmol) and then aq 30% H_2O_2 (3.42 g, 30 mmol) under argon. The mixture was stirred at 50 °C for 12 h. After cooling to room temperature, the reaction mixture was treated with water (20 mL). The mixture was extracted with Et_2O (5 × 20 mL), and the combined organic phase was washed successively with 15% aq $Na_2S_2O_3$ (20 mL). Drying over Na_2SO_4 and removal of the solvents under reduced pressure afforded the crude 1-octanol. The yield of 1-octanol was 82% as judged by capillary GC analysis using *n*-pentadecane as an internal standard.

Quenching the H_2O_2 Oxidation of 1 at the Halfway. To a mixture of KF (116 mg, 2.0 mmol) and $KHCO_3$ (200 mg, 2.0 mmol) in MeOH (2.5 mL) and THF (2.5 mL) were added **1** (248 mg, 1.0 mmol) and then aq 30% H_2O_2 (3.42 g, 30 mmol) under argon. The mixture was stirred at 50 °C for 2 h. After cooling to room temperature, the reaction mixture was treated with water (5 mL) and was extracted with Et_2O (3 × 10 mL). The aqueous phase was basified to pH 14 by adding NaOH pellet and was extracted with Et_2O (3 × 10 mL). The combined organic phase was washed successively with 15% aq $Na_2S_2O_3$ (20 mL). Drying over $MgSO_4$ and careful removal of the solvents under reduced pressure afforded the crude products. Yields of the detected products were determined as follows either by capillary GC analysis using *n*-pentadecane as an internal standard or by NMR analysis using hexamethyldisilane as an internal standard: **1** (19%, NMR), 1-octanol (51%, GC), **4** (14%, NMR), **5** (2%, NMR), and pyridine (43%, NMR).

***m*-CPBA Oxidation of 1.** To a mixture of *m*-CPBA (175 mg, 1.02 mmol) and KF (31 mg, 0.53 mmol) in DMF (1.0 mL) was added **1** (124 mg, 0.50 mmol) at room temperature under argon. After stirring for 20 h at room temperature, the reaction mixture was worked-up by the same procedure as that used for the H_2O_2 oxidation of **1**. The yield of 1-octanol was 46% as judged by capillary GC analysis using *n*-pentadecane as an internal standard.

Attempt to Convert 1 to 4. To a mixture of KF (116 mg, 2.0 mmol) and $KHCO_3$ (200 mg, 2.0 mmol) in H_2O (0.25 mL) and THF (5.0 mL) was added **1** (249 mg, 1.0 mmol) under argon. The mixture was stirred at 50 °C for 2 h. After cooling to room temperature, the reaction mixture was treated with water (5 mL) and was extracted with Et_2O (3 × 10 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded **1** (98% by GC analysis).

Attempt to Convert 1 to 5 (Table 2, entry 1). To a mixture of KF (116 mg, 2.0 mmol) and $KHCO_3$ (200 mg, 2.0 mmol) in MeOH (2.0 mL) and THF (2.0 mL) was added **1** (249 mg, 1.0 mmol) under argon. The mixture was stirred at 50 °C for 2 h. After cooling to room temperature, the reaction mixture was treated with water (5 mL) and was extracted with Et_2O (3 × 20 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded **5** (100% conversion, 72% yield by GC analysis).

Attempt to Convert 5 to 4. To a solution of KF (116 mg, 2.0 mmol) in MeOH (3.0 mL), THF (3.0 mL), and H_2O (3.0 mL) was added **5** (202 mg, 1.0 mmol) under argon. The mixture was stirred at 50 °C for 2 h. After cooling to room temperature, the reaction mixture was treated with water (5 mL) and was extracted with Et_2O (3 × 20 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded **4** (93% conversion, 92% yield by NMR analysis).

H_2O_2 Oxidation of 4 (Table 3, entry 2). To a mixture of KF (116 mg, 2.0 mmol) and $KHCO_3$ (200 mg, 2.0 mmol) in MeOH (3.0 mL) and THF (3.0 mL) were added **4** (188 mg, 1.0 mmol) and then aq 30% H_2O_2 (3.42 g, 30 mmol) under argon. The mixture was stirred at 50 °C for 5 h. After cooling to room temperature, the reaction mixture was treated with water (20 mL) and was extracted with Et_2O (5 × 20 mL). The combined organic phase was washed successively with 15% aq $Na_2S_2O_3$ (20 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded the crude 1-octanol. The yield of 1-octanol was 76% as judged by capillary GC analysis using *n*-pentadecane as an internal standard.

H_2O_2 Oxidation of 5 (Table 3, entry 5). To a mixture of KF (58 mg, 1.0 mmol) and $KHCO_3$ (200 mg, 2.0 mmol) in MeOH (3.0 mL) and THF (3.0 mL) was added **5** (202 mg, 1.0 mmol) and then aq 30% H_2O_2 (3.42 g, 30 mmol) under argon. The mixture was stirred at 50 °C for 5 h. After cooling to room temperature, the reaction mixture was treated with water (20 mL) and was extracted with Et_2O (5 × 20 mL). The combined organic phase was washed successively with 15% aq $Na_2S_2O_3$ (20 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded the crude 1-octanol. The yield of 1-octanol was 68% as judged by capillary GC analysis using *n*-pentadecane as an internal standard.

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