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Highly Efficient O-Silylation of Alcohol with Vinylsilane Using a Rh(I)/HCl Catalyst at Room Temperature

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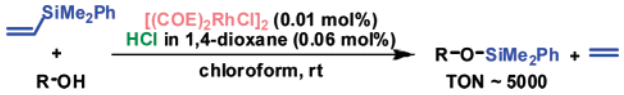
ABSTRACT



Highly efficient O-silylation of alcohol with vinylsilane was developed using a catalyst system consisting of $[(COE)_2RhCl]_2$ and HCl. In this reaction, a key intermediate is chlorosilane, generated from vinylsilane and HCl, which can be regenerated in the catalytic cycle. Various alcohols and vinylsilanes were applied to the preparation of silyl ether compounds with this catalyst system.

The O-silylation of hydroxyl groups has great potential as a protecting strategy in organic synthesis.[1] A variety of O-silylation methods for preparing silyl ether compounds from alcohols have been developed. These methods have utilized chlorotrialkylsilane,[2] hexamethyldisilazane,[3] trimethylsilyl azide,[4] trimethylsilyl cyanide,[5] allylsilane,[6] silyl methallylsulfinate,[7] etc. In addition, several efficient and environmentally benign O-silylation processes using transition-metal catalysts have been reported: dehydrogenative silylation,[8] silylation by disilane,[9] allylsilane,[6e,f] etc. However, some of these processes have limitations, including the removal of stoichiometric byproducts,[2] the instability of silane substrates toward moisture,[2−5] the requirement of high-temperature reaction conditions,[6,9] and the rarity of various silane derivatives.[3,8,9] Recently, we reported the Rh(I)-catalyzed O-silylation of alcohol with vinylsilane,[10] but this reaction requires high temperature (>100 °C). However, in the course of our studies of transition-metal-catalyzed O-silylation, we discovered a new catalytic system for O-silylation of alcohol which operates under very mild conditions. Herein, we wish to report a novel catalyst mixture, Rh(I) and HCl, for highly efficient O-silylation of alcohol with vinylsilane at room temperature. This reaction proceeds well, even in aerial conditions.

The reaction of phenethyl alcohol (**1a**, 0.5 mmol) and vinylsilane **2a** (1.5 mmol) was carried out at ambient

(1) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley and Sons: New York, 1999; p 113.
(2) (a) Morita, T.; Yoshida, S.; Okamoto, Y.; Sakurai, H. *Synthesis* **1979**, *5*, 379. (b) Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972**, *94*, 2549.
(3) (a) Zhang, Z.-H.; Li, T.-S.; Yang, F.; Fu, C.-G. *Synth. Commun.* **1998**, *28*, 3105. (b) Chrini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *Synth. Commun.* **1999**, *29*, 541. (c) Karimi, B.; Golshani, B. *J. Org. Chem.* **2000**, *65*, 7228. (d) Firouzabadi, H.; Iranpoor, N.; Amani, K.; Nowrouzi, F. *J. Chem. Soc., Perkins Trans. 1* **2002**, *23*, 2601. (e) Firouzabadi, H.; Iranpoor, N.; Sobhani, S.; Ghassamipour, S.; Amoozgar, Z. *Tetrahedron Lett.* **2003**, *44*, 891. (f) Azizi, N.; Saidi, M. R. *Organometallics* **2004**, *23*, 1457. (g) Ghosh, A. K.; Bilcer, G.; Schiltz, G. *Synthesis* **2001**, 2203. (h) List, B.; Castello, C. *Synlett* **2001**, 1687. (i) For an article of application to mesoporous silica surface, see: Zapilko, C.; Widenmeyer, M.; Nagl, I.; Estler, F.; Anwander, R.; Raudaschl-Sieber, G.; Groeger, O.; Engelhardt, G. *J. Am. Chem. Soc.* **2006**, *128*, 16266.
(4) (a) Sinou, D.; Emziane, M. *Synthesis* **1986**, 1045. (b) Amantini, D.; Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.* **2001**, *66*, 6734.
(5) Mai, K.; Patil, G. *J. Org. Chem.* **1986**, *51*, 3545.
(6) (a) Morita, T.; Okamoto, Y.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 835. (b) Olah, G. A.; Husain, A.; Gupta, B. G. B.; Salem, G. F.; Narang, S. C. *J. Org. Chem.* **1981**, *46*, 5212. (c) Hosomi, A.; Sakurai, H. *Chem. Lett.* **1981**, *1*, 85. (d) Olah, G. A.; Husain, A.; Singh, B. P. *Synthesis* **1983**, 892. (e) Suzuki, T.; Watahiki, T.; Oriyama, T. *Tetrahedron Lett.* **2000**, *41*, 8903. (f) Shibata, T, Kanda, K, Ueno, Y.; Fujiwara, R. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1146.
(7) Huang, X.; Craita, C.; Awad, L.; Vogel, P. *Chem. Commun.* **2005**, 1297.
(8) (a) For a review, see: Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265. (b) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (c) Ito, H.; Watanabe, A.; Sawamura, M. *Org. Lett.* **2005**, *7*, 1869 and references cited therein.
(9) (a) Tanabe, Y.; Okumura, H.; Maeda, A.; Murakami, M. *Tetrahedron Lett.* **1994**, *35*, 8413. (b) Shirakawa, E.; Hironaka, K.; Otsuka, H.; Hayashi, T. *Chem. Commun.* **2006**, 3927.
(10) Park, J.-W.; Chang, H.-J.; Jun, C.-H. *Synlett* **2006**, *5*, 771.

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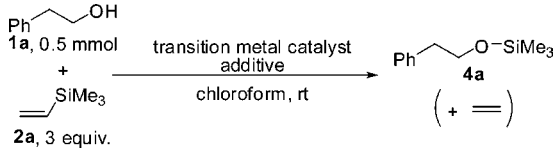
temperature for 2 h in the presence of chlorobis(cyclooctene)-rhodium dimer (**3a**, 0.5 mol % based on **1a**) and HCl (3 mol %) dissolved in 1,4-dioxane.[11] A quantitative yield (96% isolated yield) of phenethyl trimethylsilyl ether (**4a**) was obtained with the evolution of ethylene gas. In addition, some other catalyst systems for O-silylation at room temperature were investigated as shown in Table 1. No reaction occurred

Table 1. O-Silylation of **1a** with **2a** Using Various Transition Metal Catalysts[a]



entry	transition-metal catalyst/additive	amount of catalysts (mol %)	time (h)	yield (%, GC)
1	$[(COE)_2RhCl]_2$/HCl	0.5/3	2	100
2	$[(COE)_2RhCl]_2$	0.5	2	0
3	$[(C_2H_4)RhCl]_2$/HCl	0.5/3	2	100
4	$[(COD)RhCl]_2$/HCl	0.5/3	2	0
5	$[(COE)_2IrCl]_2$/HCl	1.5/9	2	83
6	$[(p\text{-cymene})_2RuCl]_2(\mu\text{-Cl})_2$/HCl	0.5/3	2	0
7	$[(C_2H_4)_2PtCl]_2(\mu\text{-Cl})_2$/HCl	0.5/3	2	0
8	$[(\eta^3\text{-}C_3H_5)PdCl]_2$/HCl	0.5/3	2	0
9	$RhCl_3{\cdot}3H_2O$	1	9	100

[a] Reaction conditions: 0.5 mmol of phenethyl alcohol, 3.0 equiv of trimethylvinylsilane, 0.5 mol % of transition-metal catalyst in 100 mg of $CHCl_3$ for 2 h at room temperature.

using the rhodium(I) catalyst **3a** in the absence of HCl (entry 2). Also, no increase of the catalytic effect was observed with an increase in the concentration of HCl, implying that a certain catalytic amount of HCl based upon **3a** is good enough for the reaction to proceed. $[(C_8H_{14})_2IrCl]_2$/HCl also showed catalytic activity with less reactivity when compared to that of $[(C_8H_{14})_2RhCl]_2$/HCl (entry 5). Other transition-metal complexes containing Ru, Pt, and Pd did not show any catalytic activity (entries 6−8). Surprisingly, $RhCl_3{\cdot}3H_2O$ (1 mol %) showed catalytic activity with a slow reaction rate; the reaction was completed in 9 h (entry 9). This result can be explained by the fact that phenethyl alcohol may reduce $RhCl_3{\cdot}3H_2O$ to Rh(I) with the generation of HCl as an active catalytic species.[12] This seems to be the reason why an induction period is required to generate the catalytic species.

In order to clarify the catalytic reaction mechanism, an attempt was made to identify an intermediate. An initially formed complex **3c**, chlorobis(trimethylvinylsilane)rhodium-(I) dimer[13] determined by ^{1}H NMR spectra (Figure 1a), was obtained by olefin exchange reaction of **3a** or **3b** with **2a**, and then **3c** was treated with an excess amount of HCl in

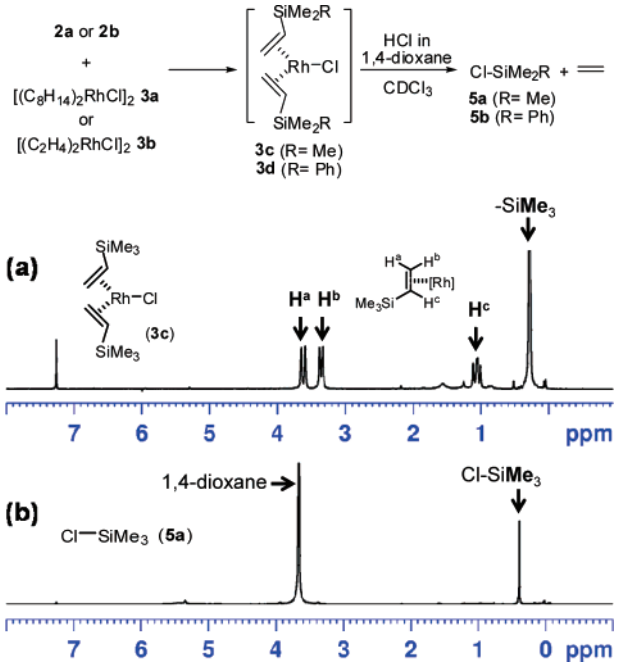


Figure 1. (a) ^{1}H NMR spectra of **3c** formed by an olefin exchange reaction of **3b** with **2a**, and (b) that of **5a** generated by the addition of HCl in dioxane to **3c**.

$CDCl_3$. In the resulting solution, chlorotrimethylsilane (**5a**) was determined as a sole product by ^{1}H NMR (Figure 1b). With **2b** (R = Ph), chlorodimethylphenylsilane (**5b**) was also identified (see Figure S1 in Supporting Information).

The mechanism of the catalytic reaction can be inferred based on the experimental evidence above. Initially, the olefin exchange reaction of cyclooctene in chlorobis(cyclooctene)-rhodium(I) dimer (**3a**) with vinylsilane leads to the formation of the chlorobis(trimethylvinylsilane)rhodium(I) dimer (**3c**). The reaction of **3c** with HCl might generate the (trimethylsilylethyl)rhodium(III) complex **7a** via **6a**,[14] followed by β-silyl elimination in **7a** to render the Rh−$SiMe_3$ complex (**8a**) containing ethylene (Scheme 1). This type of β-silyl elimination in transition-metal complexes has been recently reported.[15] Reductive elimination in **8a** results in complex **9a** and chlorotrimethylsilane (**5a**). Intermediate **5a** reacts with alcohol **1a** to give silyl ether **4a** with the regeneration of HCl, which reenters the catalytic cycle. An olefin exchange reaction of **9a** with vinylsilane **2a** leads to the formation of **3c**, liberating ethylene gas.

The reactions of various alcohols and vinylsilanes were carried out in the presence of **3a**/HCl at room temperature,

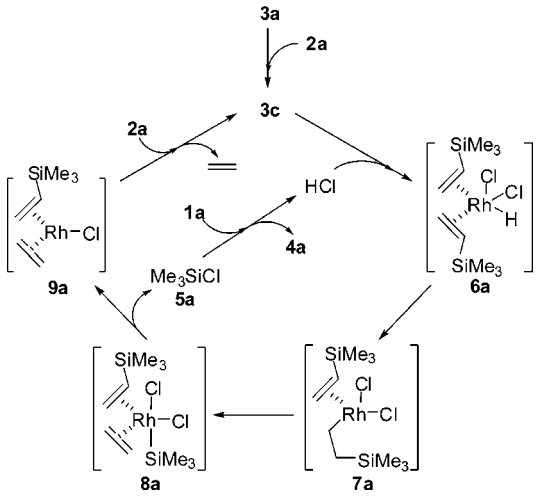
(11) Commercially available HCl dissolved in 1,4-dioxane was used without further purification.

(12) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92.

(13) Complex **3c** was prepared by olefin exchange reaction of chlorobis-(ethylene)rhodium(I) dimer (**3b**) with trimethylvinylsilane, and a crude identical spectra of **3c** could be also obtained from **3a** and **2a**. Blażejewska-Chadyniak, P.; Kubicki, M.; Maciejewski, H.; Marciniec, B. *Inorg. Chim. Acta* **2003**, *350*, 603−608.

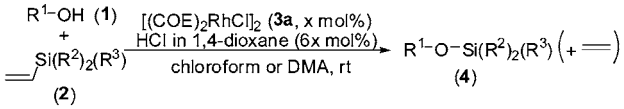
(14) For the related references of organometallic reactions incorporating an acid with transition-metal complexes, see: (a) Chung, M.-K.; Orlova, G.; Goddard, J. D.; Schlaf, M.; Harris, R.; Beveridge, T. J.; White, G.; Hallett, F. R. *J. Am. Chem. Soc.* **2002**, *124*, 10508. (b) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828. See also ref 9b.

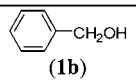
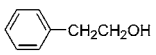
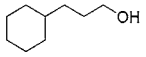
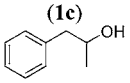
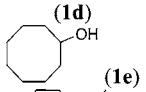
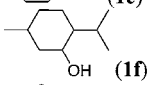
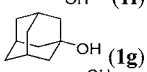
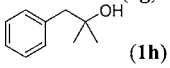
Scheme 1. Proposed Mechanism of O-Silylation of Phenethyl Alcohol (**1a**) with Trimethylvinylsilane (**2a**) Using the Catalytic System of $[(C_8H_{14})_2RhCl]_2$(**3a**)/HCl



as shown in Table 2. It was found that the reactions with 1° alcohols proceed quite well under ambient temperature. Even 2° and 3° alcohols showed good reactivity with an increased amount of catalyst. The reaction of alcohol with bulky vinylsilanes such as dimethylphenylvinylsilane and triethylvinylsilane also afforded corresponding silyl ethers in good yields (entries 3, 8, and 9).

Table 2. Reactions of Various Alcohols and Vinylsilanes[a]



entry	R^1-OH	R^2, R^3	x mol% (**3a**) / rxn time	Isolated yield(%) of **4**[b]
1	 (**1b**)	Me, Me (**2a**)	0.5 mol% / 2 h	94(100) (**4b**)
2	 (**1a**)	Me, Me (**2a**)	0.5 mol% / 2 h	96(100) (**4a**)
3		Et, Et (**2c**)	1.5 mol% / 4 h	75(100) (**4c**)
4	 (**1c**)	Me, Me (**2a**)	0.5 mol% / 4 h	97(100) (**4d**)
5	 (**1d**)	Me, Me (**2a**)	1.5 mol% / 4 h	98(100) (**4e**)
6	 (**1e**)	Me, Me (**2a**)	1.5 mol% / 4 h	96(100) (**4f**)
7	 (**1f**)	Me, Me (**2a**)	1.5 mol% / 4 h	88(96) (**4g**)
8	 (**1g**)	Me, Ph (**2b**)	2.5 mol% / 4 h	90(100)[c] (**4h**)
9	 (**1h**)	Me, Ph (**2b**)	2.5 mol% / 4 h	88(100)[c] (**4i**)

[a] Reaction conditions: 0.5 mmol of alcohol, 3.0 equiv of vinylsilane in 100 mg of $CHCl_3$ at room temperature. [b] GC yields are given in parentheses. [c] DMA is used as a solvent.

In order to identify the catalytic efficiency of this O-silylation, the reaction of dimethylphenylvinylsilane with ethanol or 2-propanol was performed in the presence of only 0.01 mol % of **3a** with 0.06 mol % of HCl at room temperature. It was found that the reactions were completed within 24 h and gave quantitative yields of corresponding silyl ethers **4j** or **4k**, corresponding to 5000 TONs (Figure 2).

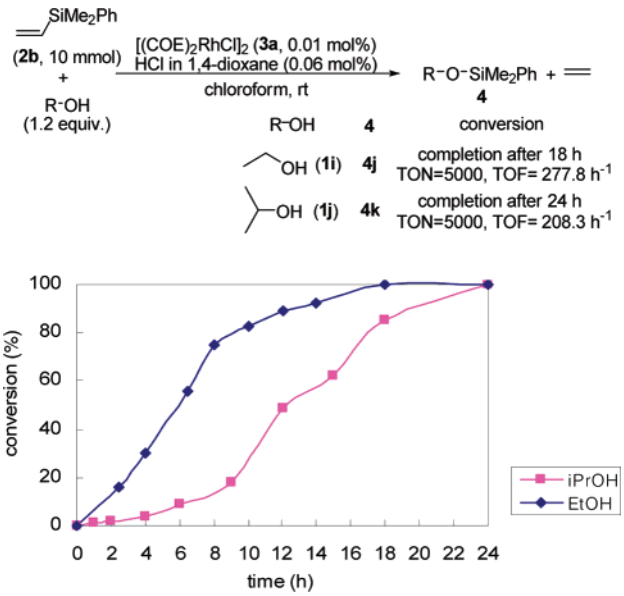


Figure 2. Conversion (yields of silyl ethers) versus time plot of the O-silylation of ethyl alcohol (**1i**) or isopropanol (**1j**) with dimethylphenylvinylsilane (**2b**) in the presence of 0.01 mol % of **3a** and 0.06 mol % of HCl.

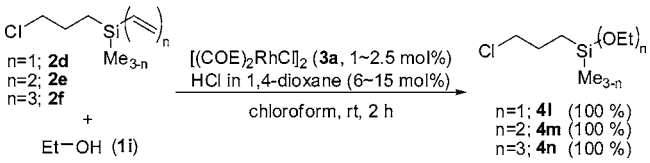
Encouraged by these results, we attempted to apply this O-silylation protocol to the synthesis of multialkoxysilanes, which can be used for the immobilization of solid supports or substrates for sol−gel processes.[16] Di- and trialkoxysilane, as well as monoalkoxysilane, were prepared by the multiple O-silylation of corresponding vinylsilanes with alcohol. One of the merits of this process is that multivinylsilanes, precursors of alkoxysilanes, can be freshly purified by column chromatography due to their inertness. Trialkoxysilanes, however, are hard to purify by this chromatographic method due to the sensitive nature of trialkoxysilane toward

(15) For the related references of β-silyl elimination in silylative coupling of vinyl or aromatic compounds: (a) Kakiuchi, F.; Tanaka, Y.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1993**, *456*, 45−47. (b) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320−4326. (c) Marciniec, B.; Walczuk-Gusciora, E.; Blazejewska-Chadyniak, P. *J. Mol. Catal. A: Chem.* **2000**, *160*, 165−171. (d) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *Organometallics* **2000**, *19*, 1677−1681. (e) Marciniec, B.; Walczuk-Gusciora, E.; Pietraszuk, C. *Organometallics* **2001**, *20*, 3423−3428. (f) Marciniec, B.; Chadyniak, D.; Krompiec, S. *Tetrahedron Lett.* **2004**, *45*, 4065−4068. (g) Kakiuchi, F.; Matsumoto, M.; Sonoda, M.; Fukuyama, T.; Chatani, N.; Murai, S. *Chem. Lett.* **2000**, *7*, 750−751.

(16) For the recent review of silica-based organic−inorganic hybrid, see: Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M.; *Angew. Chem., Int. Ed.* **2006**, *45*, 3216.

silica gel. As an example of this process, 3-chloropropyltrivinylsilane (**2f**) was prepared and purified by column chromatography. Then **2f** was allowed to react with ethanol (**1i**) in the presence of a catalytic amount of **3a** and HCl at ambient temperature for 2 h. The reaction resulted in a quantitative yield of corresponding 3-chloropropyltriethoxysilane (**4n**), determined by GC (Scheme 2). Other corresponding mono- and divinylsilanes (**2d** and **2e**) could also be transformed into monoethoxysilane **4l** and diethoxylsilane **4m** in quantitative yields using the same catalyst system. This method could be used in the future to prepare a bulky functionalized alkylalkoxysilane.

Scheme 2. Conversion of Vinylsilane to Alkoxysilane



In conclusion, we have developed a new O-silylation method using a transition-metal catalytic system: $[(C_8H_{14})_2RhCl]_2$ and HCl. The reaction proceeds quite well, even in aerial conditions. In the reaction mechanism, HCl plays an important role in initiating the reaction, and chlorosilane is a key intermediate. In this method, various alcohols and vinylsilanes could be used in the preparation of silyl ether compounds. The further application of this protocol to the synthesis of functionalized alkylalkoxysilanes is currently under study.

Acknowledgment. This paper is dedicated to the memory of the late Professor Yoshihiko Ito (1937−2006) of the University of Kyoto. This work was supported by CBMH and Grant No. R01-2005-000-10548-0 from the Basic Research Program of the Korea Science & Engineering Foundation. J.-W.P. acknowledges the fellowship of the BK21 program from the Ministry of Education and Human Resources Development and the Seoul Science Fellowship Program.

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

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