CHEMISTRY LETTERS, pp. 347-350, 1993.

Dehydrogenative Silylation of Ketones with a Bifunctional Organosilane by Rhodium-Pybox Catalysts

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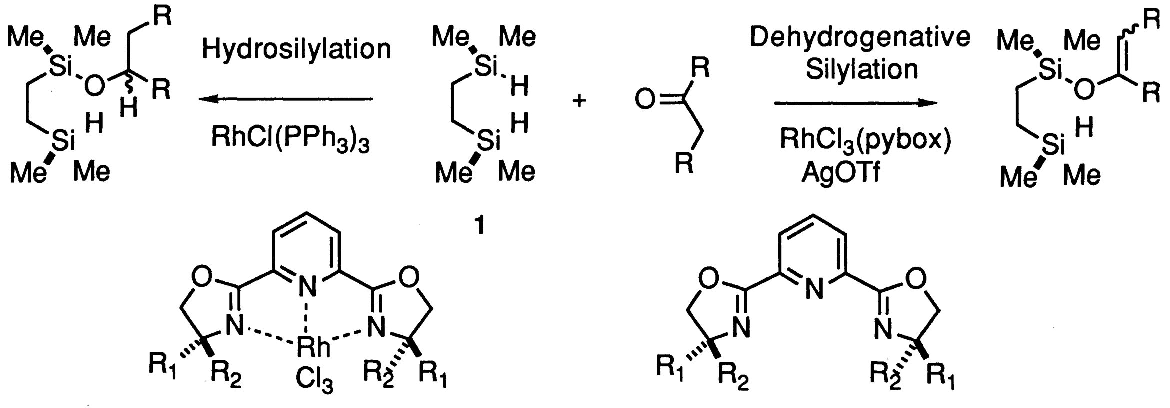
Dehydrogenative silylation of ketones with 1,2-bis(dimethylsilyl)ethane is catalyzed by a mixture of $RhCl_3$(pybox) and AgOTf to form the corresponding silylenol ether in high yields. Only one Si-H group of 1,2-bis(dimethylsilyl)ethane is converted to the corresponding silyl enol ether.

In our previous paper, we reported a $RhCl(PPh_3)_3$-catalyzed hydrosilylation of ketones with 1,2-bis(dimethylsilyl)ethane (**1**), which is more than 60 times faster than the reactions with monodentate trialkylsilanes such as Et_3SiH.[1)] Only one Si-H terminus of **1** is converted to the corresponding alkoxysilane, whereas reaction of the remaining Si-H with ketones was as slow as that with $EtMe_2SiH$. These results imply that bidentate structure of **1** contributes to rate acceleration toward hydrosilylation. On the other hand, our efforts to develop asymmetric hydrosilylation of ketones revealed that a mixture of $RhCl_3$(iPr-Pybox) (**2b**) and Ag^+ salts is an efficient catalyst to achieve the highly asymmetric formation of the corresponding alkoxysilanes in the presence of silver salts.[2)] As an extension of these two results, we were interested in the



$RhCl_3$(Pybox)

2a; $R_1 = R_2 = Me$

2b; $R_1 = H$, $R_2 = {}^iPr$

Pybox

3a; $R_1 = R_2 = Me$

3b; $R_1 = H$, $R_2 = {}^iPr$

Scheme 1.

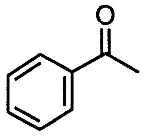
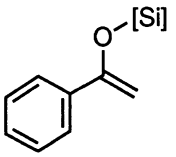
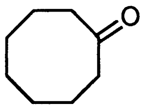
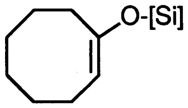
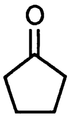
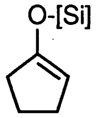
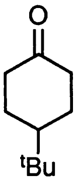
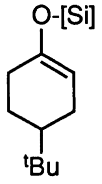
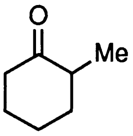
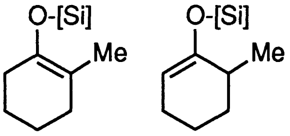
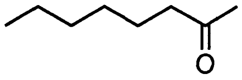
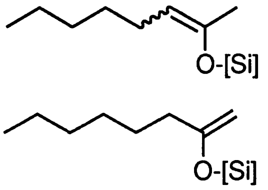
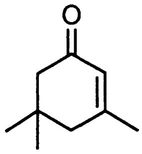
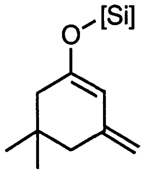
reaction of ketones with **1** by the Rh-Pybox catalysts, **2a** or **2b**. The reaction successfully occurred at 50°C, being terminated after only one Si-H terminus of **1** was consumed. However, the product was not alkoxysilane derived from the hydrosilylation but enol silyl ethers from the dehydrogenative silylation as shown in Scheme 1.3) Attempted reactions with unidentate trialkylsilanes such as $PhMe_2SiH$ and $EtMe_2SiH$ under the same conditions failed, suggesting that the bidentate structure of **1** is crucially important for the achievement of the reaction.

The dehydrogenative silylation proceeded by a 1 : 2 mixture of **2a** or **2b** and AgOTf in CH_2Cl_2 at 50 °C under an inert gas atmosphere. Addition of 2-4 equivalent of the pybox ligand, **3a** or **3b**, to the catalyst raised the yield of enol silyl ethers. THF can be used as an alternative solvent in the reaction with **2b**. Generation of cationic rhodium species from **2a** or **2b** by AgOTf is essentially important for the dehydrogenative silylation; slow hydrosilylation proceeded over 50°C in its absence. In a typical example, to a mixture of **2a** (0.3 mmol), AgOTf (0.6 mmol), and **3a** (1.2 mmol) in CH_2Cl_2 (2 mL) was added **1** (6 mmol), and acetophenone (6 mmol), and the mixture was heated under reflux for 3 h. After removal of the solvent, the residue was purified by a silica-gel column deactivated by Et_3N eluting by hexane to give the corresponding enol silyl ether. [Colorless oil. ^1H NMR (270 MHz, $CDCl_3$) d 0.05 (d, 6H, J = 3.1 Hz, $SiHMe_2$), 0.23 (s, 6H, $OSiMe_2$), 0.53-0.72 (m, 4H, $SiCH_2$), 3.81 (sep, 1H, J = 4.5 Hz, SiH), 4.40 and 4.88 (two d, 1H, J = 1.5 Hz, olefin), 7.31-7.59 (m, 5H, Ph). ^{13}C NMR (67.8 MHz, $CDCl_3$) d -4.9 and -2.2 (SiMe), 5.6 and 9.4 ($SiCH_2$), 90.9 ($\mathit{C}H_2{=}C$), 125.2, 125.3, 128.0 and 128.2 (phenyl), 130.1 ($CH_2{=}\mathit{C}$). IR (neat) 2120 (SiH), 1620 ($CH_2{=}C$). Anal. Found: C, 64.32; H, 11.69%. Calcd for $C_{15}H_{24}OSi_2$: C, 64.12; H, 11.17%.]

Other ketones shown in Table I underwent the dehydrogenative silylation under the similar conditions. The reaction contributes to regioselective preparation of silyl enol ethers from unsymmetrical ketones as shown in entries 5-6. More substituted silyl enol ethers, which are thermodynamically more stable than the others,4) were formed predominantly in each case. Regioselective formation of thermodynamically stable isomer of silyl enol ether of 2-methylcyclohexanone was also observed in the cobalt-catalyzed dehydrogenative silylation reported by Sakurai and coworkers.3) The reaction of isophorone with **1** gave dienol silyl ether. Despite possible formation of other isomers, one dienol silyl ether shown in entry 7, which is also a thermodynamically stable isomer,5) was selectively formed.

It is known that reactions of bidentate organosilanes with a stoichiometric amount of several transition metal complexes provided the corresponding disilametallacyclic complexes with evolution of molecular hydrogen.6) However, catalytic reactions of bidentate organosilanes, which cannot be achieved with unidentate silanes, have not been developed until recently.1,7-9) Dehydrogenative silylation of keteones presented in this paper does not occur with unidentate trialkylsilanes or Ph_2SiH_2,2) unequivocally showing the importance of the bidentate structure of **1**. On the other hand, achievement of selective dehydrogenative silylation of ketones by rhodium-pybox catalysts is in sharp contrast to the results that rhodium-phosphine catalysts are generally active for the hydrosilylation of ketones. Further mechanistic10,11) and synthetic studies12) are in progress.

Table I. Dehydrogenative silylation of ketones with Rh-pybox catalysts a)

Entry	Substrate	Catalyst	Time/h	Yield/%	Product
1		**2a** **2b**	3 3	80 71	
2		**2a** **2b**	7 5	61 96	
3		**2a**	4	83	
4		**2b**	2.5	80	
5		**2b**	3	97	 79 : 21
6		**2a**	3.5	67	 78 : 22
7		**2a** **2b**	1.5 4.5	90 95	

a) All reactions were carried out with the catalyst (**2a** or **2b**; 0.5 mol%), AgOTf (1 mol%), and an additional ligand (**3a** or **3b**; 2 mol%) at 40-50 ˚C. The reaction with **2a** was carried out in THF, whereas that with **2b** was done in CH_2Cl_2.

Financial supports from Ministry of Education, Science, and Culture, for a Grant-in-Aid for Scientific Research (02247210, 03233212, and 042172212) and from Ishida Foundation (90-502) are acknowledged.

References

1) H. Nagashima, K. Tatebe, T. Ishibashi, J. Sakakibara, and K. Itoh, *Organometallics*, **8**, 2495 (1989).

2) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo, and K. Itoh, *Organometallics*, **8**, 846 (1989); H. Nishiyama, M. Kondo, T. Nakamura, and K. Itoh, *ibid.*, **10**, 500 (1991).

3) Other transition metal-catalyzed dehydrogenative silylations; H. Sakurai, K. Hosaka, T. Sawahata, Y. Watanabe, and K. Iguchi, *Tetrahedron Lett.*, **31**, 2671 (1977); I. Ojima and Y. Nagai, *J. Organomet. Chem.*, **57**, C42 (1973); E. Frainnet, Y. Martel-Siegfried, E. Brousse, and J. Dedier, *ibid.*, **85**, 297 (1975)

4) G. Stork and P. F. Hundrlik, *J. Am. Chem. Soc.*, **90**, 4462, 4464 (1968); H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969); H. O. House, M. Gall, and H. D. Olmstead, *ibid.,* **36**, 2361 (1971).

5) M. Kawanishi, Y. Itoh, T. Hieda, S. Kojima, T. Hitomi, and K. Kobayashi, *Chem. Lett.*, **1985**, 647.

6) W. Fink, *Helv. Chim. Acta.*, **57**, 1010 (1974); **59**, 606 (1976); R. J. P. Corriu, J. Moreau, and M. Pataud-Sat, *Organometallics*, **4**, 623 (1985); L. Varcea and W. A. G. Graham, *Inorg. Chem.,* **13**, 511 (1974).

7) H. Nagashima, K. Tatebe, and K. Itoh, *J. Chem. Soc., Perkin Trans. I,* **1989**, 1807.

8) Y. Uchimaru, H. J. Lautenschlager, A. J. Eynd, M. Tanaka, and M. Goto, *Organometallics*, **11**, 2639 (1992); M. Tanaka, Y. Uchimaru, and H. J. Lautenschlager, *J. Organomet. Chem.*, **428**, 1 (1992); R. N. Prabhakar, Y. Uchimaru, H. J. Lautenschlager, and M. Tanaka, *Chem. Lett.*, **1992**, 45; M. Tanaka, Y. Uchimaru, and H. J. Lautenschlager, *Organometallics*, **10**, 16 (1991).

9) R. J. P. Corriu, J. Moreau, and M. Pataus-Sat, *J. Organomet. Chem.*, **228**, 301 (1982).

10) Facile reaction of bidentate organosilane may suggest involvement of Rh(V) intermediates such as $H_2Rh(V)\text{-}SiMe_2(CH_2)_2SiMe_2$.[11]

11) Recent mechanistic proposals of Rh-catalyzed hydrosilylation of unsaturated molecules. A. Millan, M.-J. Fernandez, and P. M. Bentz, *J. Mol. Cat.*, **26**, 89 (1984); S. B. Duckett and R. N. Perutz, *Organometallics,* **11**, 90 (1992).

12) Easily accecible chiral pybox ligands may provide us a new asymmetric synthesis of enol silyl ethers. As a preliminary experiment, optically active silyl enol ether of 4-t-butylcyclohexanone was formed in 7% ee, whereas kinetic resolution of 2-t-butylcyclohexanone providing 11% ee of 2-t-butylcyclohexanone after 60% conversion. Asymmetric synthesis of trimethylsilyl enol ether of t-butylcyclohexanone; D. Sato, H. Kawasaki, I. Shimada, Y. Arata, K. Okamura, T. Date, and K. Koga, *J. Am. Chem. Soc.*, **114**, 761 (1992).

(Received November 30, 1992)