# Rhodium-catalyzed Addition of Aryl- and Alkenylsilanediols to Aldehydes

Toshinari Fujii, Tooru Koike, Atsunori Mori,* Kohtaro Osakada

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan
Fax +81(45)9245224; E-mail: amori@res.titech.ac.jp

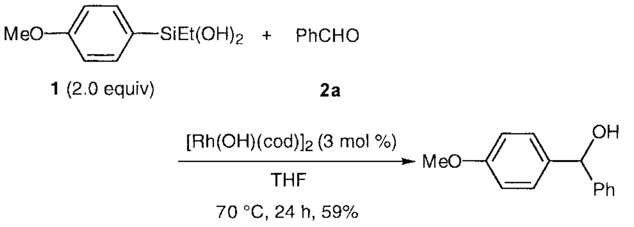
*Received 14 November 2001*

**Abstract:** Arylation and alkenylation of aromatic aldehydes with silanediols is shown to proceed by use of a catalytic amount of rhodium complex. Treatment of ethyl(4-methoxyphenyl)silanediol with benzaldehyde in the presence of 3 mol% of $[Rh(OH)(cod)]_2$ affords 4-methoxyphenyl(phenyl)methanol in 59% yield after stirring at 70 °C for 24 hours. On the other hand, diarylketone was also obtained at elevated temperature via β-hydride elimination from intermediary rhodium alkoxide.

**Key words:** silanediol, rhodium complex, arylation, alkenylation, aldehyde

Nucleophilic addition of aryl- and alkenyl-metal reagents to carbonyl compounds has been a fundamental reaction in organic synthesis. By contrast to the highly reactive organometallic nucleophilic reagents such as lithium or magnesium, use of an organosilicon reagent has rarely been studied so far.[1–3] We have recently been studying the synthetic application of silanols, a new class of organosilicon reagent bearing hydroxy groups on the silicon atom, and revealed that the carbon-silicon bond of silanols successfully affect several carbon-carbon bond-forming reactions by the catalysis of a transition metal complexes.[4] Indeed, we reported that organosilicon reagents bearing hydroxy groups on the silicon atom affect Mizoroki–Heck (MH) type reaction and conjugate addition to α,β-unsaturated carbonyl compounds in the presence of a catalytic amount of a rhodium complex.[5] Hence, we envisaged the addition of such aryl- and alkenylsilanediols to aldehydes with the rhodium catalyst.

The reaction of ethyl(4-methoxyphenyl)silanediol (**1**) with benzaldehyde (**2a**) was carried out in the presence of 3 mol% of $[Rh(OH)(cod)]_2$ in THF at 70 °C, which conditions were similar to those for the MH-type reaction of α,β-unsaturated carbonyl compounds.[5] The corresponding secondary alcohol was obtained in 59% yield after stirring for 24 hours as shown in the Equation.



**Equation**

The table summarizes the results on the rhodium-catalyzed reactions of several aldehydes and silanediols. The reaction with twice molar amounts of silanediol to aldehyde was found to be optimum. A cationic rhodium complex, $[Rh(cod)(CH_3CN)_2]BF_4$ similarly catalyzed the addition reaction. However, addition of several phosphines as a ligand of the rhodium complex inhibited the reaction. A polar and non-aqueous solvent such as THF, DME, or 1,4-dioxane was found to be excellent, while use of water as co-solvent resulted in no reaction by contrast to the related reaction with boronic acid.[3a–c] A protic solvent, MeOH was also found to be uneffective. Aromatic aldehydes bearing an electron-donating or -withdrawing group **2b**–**e** both afforded the corresponding secondary alcohols in better yields than benzaldehyde (**2a**). The reaction of ethyl(4-methoxyphenyl)silanediol (**1**) with various aromatic aldehydes also resulted in giving good yields. In addition to arylsilanediols, the use of alkenylsilanediol **4** afforded the corresponding allylic alcohol in 79% yield. On the other hand, the reaction with aliphatic aldehydes (**2h**) was found to be unsuccessful.

Oi and Inoue recently reported that aryldifluorosilanes also reacted with aldehyde in the presence of KF as an activator.[2] By contrast, the present rhodium-catalyzed reaction with silanediol proceeded without additive, suggesting superior reactivity of silanediols to fluorosilanes. The difference would be caused by the electron donation of the oxygen atom to the d-orbital of silicon in addition to the negative inductive effect of oxygen. Such electronic effects would result in activating the carbon-silicon bond of silanediol to facilitate transmetalation of the organic group toward the rhodium catalyst. A related substituent effect of the hydroxy group, was also proposed recently by Li in the rhodium-catalyzed reactions of organostannanes.[6]

It should be pointed out that a considerable amount of diarylketone was obtained along with the desired secondary alcohol when the reaction was carried out at 100 °C in 1,4-dioxane as shown in the Scheme. The findings suggest that an addition-elimination reaction takes place as observed in the Mizoroki–Heck-type reaction of α,β-unsaturated carbonyl compounds.[7] Since no ketone was obtained in the reaction at 70 °C in 1,4-dioxane at all, the pathway to ketone would be the influence of a higher reaction temperature. The formation of diarylketone was particularly remarkable in the reaction with a silanediol

Synlett 2002, No. 2, 01 02 2002. Article Identifier:
1437-2096,E;2002,0,02,0298,0300,ftx,en;Y23201ST.pdf.

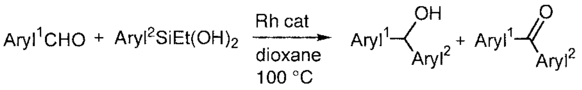
ISSN 0936-5214

**Table** Rhodium-catalyzed Addition of Silanediols to Aldehydes[a]

| Silanediol | Aldehyde | Solvent | Temp. (°C) | Yield[b] (%) |
|---|---|---|---|---|
| 4-MeO-$C_6H_4SiEt(OH)_2$ (**1**) | $C_6H_5CHO$ (**2a**) | THF | 70 | 59[c] |
| | | THF–$H_2O$ (4:1) | | 0 |
| | | MeOH | 60 | 0 |
| | | THF | 70 | 47[c,d] |
| | | DME | 80 | 68 |
| $C_6H_5SiEt(OH)_2$ (**3**) | | THF | 70 | 53[c] |
| **1** | MeO-$C_6H_4CHO$ (**2b**) | | | 66 |
| | | 1,4-dioxane | | 57 |
| | 4-$O_2N$-$C_6H_4CHO$ (**2c**) | THF | | 99 |
| | | | | 76[e] |
| | 4-MeOCO-$C_6H_4CHO$ (**2d**) | | | 91 |
| | 4-NC-$C_6H_4CHO$ (**2e**) | | | 93 |
| | 2-Naphthaldehyde (**2f**) | | | 90 |
| (*E*)-$C_6H_5CH{=}CHSiMe(OH)_2$ (**4**) | **2c** | THF | 70 | 79 |
| **1** | 2-Furaldehyde (**2g**) | 1,4-dioxane | 100 | 64 |
| | *cyclo*-$C_6H_{11}CHO$ (**2h**) | | | <5 |

[a] Unless otherwise noted, the reaction was carried out using 0.3 mmol of aldehyde and 0.6 mmol of silanediol and 0.009 mmol of $[Rh(OH)(cod)]_2$ in 2 mL of solvent.
[b] Isolated yield after silica gel chromatography was shown.
[c] The yield was estimated by $^1H$ NMR.
[d] $[Rh(cod)(CH_3CN)_2]BF_4$ (0.009 mmol) was employed instead of $[Rh(OH)(cod)]_2$.
[e] Silanediol **1** (0.36 mmol) was employed.

and/or an aldehyde bearing the electron-donating methoxy group. The reaction of aldehyde and silanediol both with methoxy groups resulted in giving 47% of the secondary alchohol and 23% of diarylketone, respectively,[8] while the yield of diarylketone was only 5% in the reaction with benzaldehyde or 4-nitrobenzaldehyde. These phenomena well correspond to the case for the reaction of α,β-unsaturated carbonyl compounds giving the 1,4-conjugate adduct and the MH-type product on the basis of electronic characteristics of the carbonyl moiety.[5]



| Aryl¹ | Aryl² | %yield | %yield |
|---|---|---|---|
| MeO-$C_6H_4$- | MeO-$C_6H_4$- | 47 | 23 |
| $C_6H_5$- | | 75 | 6 |
| 4-$NO_2$-$C_6H_4$- | | 87 | 5 |
| MeO-$C_6H_4$- | $C_6H_5$- | 53 | 8 |

**Scheme**

In summary, silanediols were found to add to aromatic aldehydes affording secondary alcohols in the presence of rhodium complexes as a catalyst. On the other hand, diarylketone was obtained at the elevated temperature accompanied by the usual addition reaction. Further studies on the mechanistic aspect and control of the reaction course are now in progress.

### Experimental Procedure for the Rhodium-catalyzed Addition of Silanediol to Aldehydes: Reaction of 1 and 2c

To a solution of ethyl(4-methoxyphenyl)silanediol (**1**) (119 mg, 0.6 mmol), 4-nitrobenzaldehyde (**2c**) (45 mg, 0.3 mmol) and $[Rh(OH)(cod)]_2$ (4.1 mg, 0.009 mmol) were dissolved in THF under an argon atomosphere. Stirring was continued at 70 °C for 24 hours and the resulting mixture was concentrated and subjected to column chromatography on silica gel (hexane–ethyl acetate, 5:1–3:1) to afford 77 mg of 4-methoxyphenyl(4-nitrophenyl)methanol (99%).

## Acknowledgement

This work was supported by a Grant-in-aid for Scientific Research (No. 13650915) from Japan Society for the Promotion of Science.

## References

(1) (a) Effenberger, F.; Spiegler, W. *Chem. Ber.* **1985**, *118*, 3872. (b) Effenberger, F.; Spiegler, W. *Chem. Ber.* **1985**, *118*, 3900. (c) Mills, R. J.; Taylor, N. J.; Snieckus, V. *J. Org. Chem.* **1989**, *54*, 4372.

(2) Oi, S.; Moro, M.; Inoue, Y. *Organometallics* **2001**, *20*, 1036.

(3) Related reactions with boron or tin: (a) Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem. Int. Ed.* **1998**, *37*, 3279. (b) Ueda, M.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 4450. (c) Ueda, M.; Miyaura, N. *J. Organomet. Chem.* **2000**, *595*, 31. (d) Oi, S.; Moro, M.; Inoue, Y. *Chem. Commun.* **1997**, 1621. (e) Oi, S.; Moro, M.; Fukuhara, H.; Kawanishi, T.; Inoue, Y. *Tetrahedron Lett.* **1999**, *40*, 9259. (f) Li, C.-J.; Meng, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9538. (g) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976. (h) Hayashi, T.; Ishigedani, M. *Tetrahedron* **2001**, *57*, 2589.

(4) (a) Hirabayashi, K.; Nishihara, Y.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 7893. (b) Hirabayashi, K.; Ando, J.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1409. (c) Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Org. Lett.* **1999**, *1*, 299. (d) Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 5342. (e) Hirabayashi, K.; Kondo, T.; Toriyama, F.; Nishihara, Y.; Mori, A. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 749. For a review: (f) Hirabayashi, K.; Mori, A. *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 926.

(5) Mori, A.; Danda, Y.; Fujii, T.; Hirabayashi, K.; Osakada, K. *J. Am. Chem. Soc.* **2001**, *123*, 10774.

(6) Huang, T.; Meng, Y.; Venkatraman, S.; Wang, D.; Li, C.-J. *J. Am. Chem. Soc.* **2001**, *123*, 7451.

(7) Mizoroki–Heck reaction of carbonyl and the related compounds: (a) Ishiyama, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 12043. (b) Hirao, T.; Misu, D.; Agawa, T. *J. Am. Chem. Soc.* **1985**, *107*, 7179.

(8) **Experimental**: To a mixture of ethyl(4-methoxyphenyl)silanediol(**1**) (119 mg, 0.6 mmol) and $[Rh(OH)(cod)]_2$ (4.1 mg, 0.009 mmol) in 2 mL of 1,4-dioxane under argon atomosphere was added 4-methoxybenzaldehyde (0.037 mL, 0.3 mmol). Stirring was continued at 100 °C for 24 h and the resulting mixture was concentrated and subjected to column chromatography on silica gel (hexane–ethyl acetate, 20:1–3:1) to afford 35 mg of bis(4-methoxyphenyl)methanol (47%) and 17 mg of 4,4'-dimethoxybenzophenone (23%). ($R_f$ = 0.22 and 0.35, respectively with Hexane–EtOAc, 3:1).