ORGANIC LETTERS

1999
Vol. 1, No. 2
299−301

A New Transformation of Silanols. Palladium-Catalyzed Cross-Coupling with Organic Halides in the Presence of Silver(I) Oxide

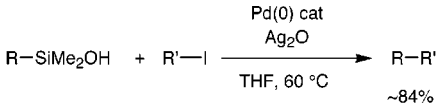
Kazunori Hirabayashi, Jun Kawashima, Yasushi Nishihara, Atsunori Mori,* and Tamejiro Hiyama[†]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Yokohama 226-8503, Japan

amori@res.titech.ac.jp

Received April 22, 1999

ABSTRACT



The reactions of aryl- and alkenylsilanols with organic halides are found to proceed in a catalyst system of 5 mol % of $Pd(PPh_3)_4$ and Ag_2O (1 equiv) to give the corresponding coupling products in up to 84% yield.

Little attention has been paid to synthetic utilization of silanols, since syntheses and isolation of silanols are considered to be difficult due to their instability to moisture, heat, acid, and base. We have recently reported a facile synthesis of silanols that possess a functional group by alkylative cleavage of a cyclic siloxane with organolithium reagents.[1,2] Functional group transformations of the obtained silanols are also documented: cyclopropanation of alkenylsilanols, for example, under the conditions of the Simmons−Smith reaction using $Et_2Zn-CH_2I_2$ is accelerated as observed with allylic alcohols.[1,3]

Our continuing interest has been focused on transformation of a carbon−silicon bond of a silanol to a carbon−carbon bond. We herein describe that cross-coupling of silanols with organic halides is realized by the addition of Ag_2O as an activator.

The cross-coupling reaction is a facile method to form a carbon−carbon bond using various organometallic reagents and organic electrophiles. Organosilicon compounds have also been revealed to undergo the cross-coupling reaction.[4] However, the coupling of arylsilanes, for example, requires the use of organosilanes with two fluorine atoms as substituents[5,6] and of a fluoride ion as an activator. Hence, an

[†] Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-8501, Japan.

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(5) Coupling reaction of $PhSiF_3$, $PhSi(alkyl)F_2$, or $PhSi(Me)_2F$ with 4-iodoacetophenone afforded the corresponding coupling product in 0% (24 h), 68−87% (12 h), or 15% (24 h) yield, respectively: Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Chem. Lett.* **1989**, 1711−1714.

(6) In the reaction of an alkenylsilane, by contrast, the monofluorosilane, alkenyl(dimethyl)fluorosilane, is also effective along with alkenyl(methyl)-difluorosilane: Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, *54*, 268−270.

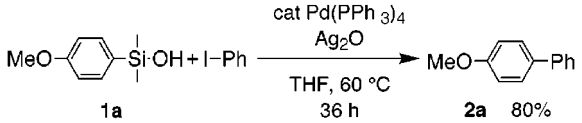
10.1021/ol990614c CCC: $18.00
Published on Web 05/27/1999

organic silanol with a single heteroatom substituent on silicon would be a facile and practical organosilicon reagent as a cross-coupling agent.[7]

The Pd(0)-catalyzed cross-coupling of a silanol was first carried out using 4-methoxyphenyl(dimethyl)silanol (**1a**) with iodobenzene in the presence of tetrabutylammonium fluoride as an additive under conditions similar to those for difluoro(ethyl)phenylsilane.[4a] However, the reaction did not occur. Conversion of the silanol into the corresponding disiloxane took place along with the recovery of iodobenzene.

Among the various additives examined, we found that the coupling reaction occurred when Ag_2O was employed as an activator.[8] For example, the reaction of **1a** with iodobenzene in THF at 60 °C for 36 h afforded 4-methoxybiphenyl (**2a**) in 80% yield as shown in Scheme 1.

Scheme 1



Although other metal oxides such as CuO, CaO, and BaO have been examined, no reaction occurred under the similar conditions. On the other hand, the reaction with several silver salts resulted in lower yields (AgOTf, 21%; $AgBF_4$, 23%; $AgNO_3$, 16%).

As a result, we currently consider that the role of Ag_2O is a base to activate the organosilicon reagent as suggested in a coupling reaction of arylboronic acid.[7] Moderate solubility of the silver salt to the reaction system would be favorable to avoid the generation of excess amounts of activated organosilicon species, which would be subjected to decompositon during the reaction. Accordingly, an appropriate amount of the thus activated silanol can participate in the catalytic cycle with the palladium complex resulting in a good yield.

Table 1 summarizes the results of the cross-coupling reactions of **1a** with iodobenzene using several solvents. The reactions proceeded in an ethereal solvent; by contrast, an aprotic polar solvent such as DMF or DMSO appeared inferior.

Table 1. Cross-Coupling of **1a** with Iodobenzene in Several Solvents[a]

entry	solvent	temp/°C	yield/%
1	THF	60	52
2	Bu_2O	100	60
3	dioxane	100	63
4	DMF	100	35
5	DMSO	100	7

[a] Reaction conditions: solvent (2 mL), **1a** (0.24 mmol), halide (0.2 mmol), $Pd(PPh_3)_4$ (5 mol %), Ag_2O (0.2 mmol), reaction time (5 h).

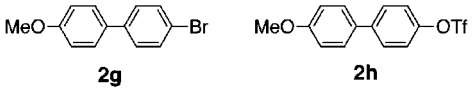
The reactions of aryl- and alkenylsilanols with a variety of organic halides are summarized in Table 2. The use of 10 mol % of Ag_2O for the reaction of **1a** with iodobenzene afforded **2a** in 17% yield (entry 2). Thus, the reaction requires a stoichiometric amount of Ag_2O. However, the use of excess (200 mol %) amounts showed little advantage (entry 3). The reactions of bromobenzene and phenyl trifluoromethanesulfonate proceeded in much lower yields (Br, 2%; OTf, 1%) under similar conditions (entries 5 and 6).

Table 2. Pd(0)-Catalyzed Reaction of Silanols with Various Halides in the Presence of Ag_2O[a]

entry	silanol		halide	time/h	Ag_2O/mol %	product	yield/%
1	4-$MeOC_6H_4SiMe_2OH$	(**1a**)	C_6H_5I	36	100	(**2a**)	80
2				65	10		17
3				38	200		84
4				5	100		52
5			C_6H_5Br				2
6			C_6H_5OTf				1
7			4-MeC_6H_4I	36		(**2b**)	75
8			2-MeC_6H_4I			(**2c**)	67
9			4-$MeCOC_6H_4I$			(**2d**)	50
10			4-$CF_3C_6H_4I$			(**2e**)	54
11			4-$O_2NC_6H_4I$			(**2f**)	45
12			4-BrC_6H_4I			(**2g**)	60
13			4-$TfOC_6H_4I$			(**2h**)	55
14	4-$CF_3C_6H_4SiMe_2OH$	(**1b**)	4-$MeOC_6H_4I$			(**2i**)	84
15	2-$MeC_6H_4SiMe_2OH$	(**1c**)				(**2j**)	30
16	(*E*)-$C_6H_5CH{=}CHSiMe_2OH$	(**1d**)				(**2k**)	80
17	(*E*)-$^nC_6H_{13}CH{=}CHSiMe_2OH$	(**1e**)				(**2l**)	69
18	4-$MeOC_6H_4SiMe_2OH$	(**1a**)	$C_6H_5CH_2Br$	14		(**2m**)	55

[a] Unless otherwise noted, the reactions were carried out under the following conditions: THF (2 mL), silanol (0.24 mmol), halide (0.2 mmol), $Pd(PPh_3)_4$ (5 mol %), and Ag_2O (0.2 mmol), at 60 °C.

The reactions of 4-iodotoluene and 2-iodotoluene proceeded in good yields (entries 7 and 8). In contrast, the use of substrates with an electron-withdrawing group resulted in relatively lower yields (entries 9−11). It is noteworthy that the reactions of 1-bromo-4-iodobenzene and 4-iodophenyl triflate afforded the corresponding products **2g** and **2h** (entries 12 and 13), respectively (Figure 1).



2g **2h**

Figure 1. Products of the reactions of 1-bromo-4-iodobenzene or 4-iodophenyl triflate with **1a**.

Other silanols similarly underwent the cross-coupling reactions in moderate to good yields. The reaction of silanol **1b** bearing an electron-withdrawing trifluoromethyl group with 4-methoxyiodobenzene proceeded in a good yield (entry 14). However, a sterically hindered silanol, dimethyl(2-methylphenyl)silanol (**1c**), gave the product in a lower yield (entry 15).

Alkenylsilanols **1d** and **1e** underwent the reactions to afford the corresponding products in good yields (entries 16 and 17). In addition, benzyl bromide also reacted with **1a** to give the diphenylmethane derivative **2m** in 55% yield (entry 18).

In summary, the palladium-catalyzed cross-coupling of silanols was achieved by the addition of Ag_2O as an activator. It is remarkable that a single hydroxy substituent effects the transformation of an aryl or alkenyl group on silicon forming a carbon−carbon bond through cross-coupling by activation with Ag_2O. Because silanols can be prepared by the cleavage of cyclic siloxanes with an organolithium reagent or careful hydrolyses of the corresponding chlorosilanes, the present coupling reaction should have great synthetic potential.

Acknowledgment. The authors are indebted to the Yamada Science Foundation for financial support. This work was also supported in part by Grants-in-Aid for Scientific Research Nos. 07405042 and 09239102 from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Experimental procedures for the preparation of arylsilanols and for the cross-coupling of the silanols. This material is available free of charge via the Internet at http://pubs.acs.org.

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