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# Silylation of primary alcohols with recyclable ruthenium catalyst and hydrosilanes

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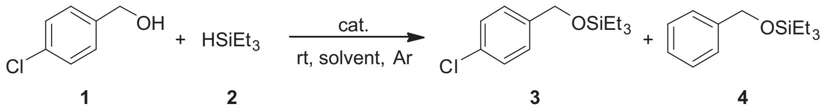
ABSTRACT

The silylation of primary alcohols was achieved using hydrosilanes and a recyclable ruthenium catalyst without additives under mild conditions. Notably, this catalyst system is effective for the silylation of alcohols having haloaryl groups, which were intact during the silylation.

The silylation of alcohols is an essential and frequent reaction for the synthesis of organosilicon compounds and for the protection of reactive hydroxyl groups in multi-step organic synthesis.[1] Usually, the silylation is carried out using chlorosilanes,[2] which requires a stoichiometric amount of a base. Transition metal-catalyzed silylation using hydrosilanes is an attractive alternative method,[3] and several catalysts have been reported such as Rh(II) carboxylates,[4a] a chip-type Rh(I) catalyst,[4b] alumina-supported gold nanoparticles,[5] colloidal palladium nanoparticles,[6] $Re_2(CO)_{12}$,[7] Grubbs' catalyst $[Cl_2(PCy_3)_2Ru=CHPh]$,[8] iridium complexes,[9] Cu(I) complexes,[10] and $[RuCl(p\text{-cymene})]_2$.[11] They have been applied for the silylation of alcohols having various functional groups such as alkenes, alkynes, alkyl halides, ketones, aldehyde, conjugated enones, esters, and carbamates.[10a,11,12] However, most of them are homogeneous catalysts which are not easy to recover. There are few examples of recycling catalysts.[4] Recovery has been demonstrated for dirhodium(II) perfluorocarboxylates bearing long perfluoroalkyl chains through fluorous separation.[4a] A chip-type Rh(I) catalyst attached to phosphane-functionalized gold surface is a notable example that showed high activity and reusability in the silylation of primary alcohols, although the reactions were performed in micromol scale.[4b] The catalytic silane alcoholysis has been achieved using alumina-supported gold nanoparticles without additional ligands at 100–110 °C. However, a recycling test has not been carried out for this heterogeneous catalyst.[5]

**Table 1**
Silylation of 4-chlorobenzyl alcohol with triethylsilane[a]



| Entry | Catalyst (mol %) | Solvent | Time (h) | Yield[b] (%) | |
|---|---|---|---|---|---|
| | | | | 3 | 4 |
| 1[c] | Pd/C (0.20) | Toluene | 3 | 57 | 38 |
| 2[c] | $Pd/Al_2O_3$ (0.20) | Toluene | 10 | 69 | 25 |
| 3 | Ru/C (3.0) | Toluene | 24 | 21 | 0 |
| 4 | $Ru/Al_2O_3$ (3.0) | Toluene | 24 | 19 | 0 |
| 5 | **1** (3.0) | Toluene | 24 | 91 | 0 |
| 6 | **1** (3.0) | Hexane | 24 | 80 | 0 |
| 7 | **1** (3.0) | Diethyl ether | 24 | 51 | 0 |
| 8 | **1** (3.0) | $CH_2Cl_2$ | 24 | 62 | 0 |

[a] The reaction was performed on 1.0 mmol of 4-chlorobenzyl alcohol and 1.2 mmol of triethylsilane with a catalyst at 25 °C under Ar atmosphere.
[b] Determined by GC with an internal standard.
[c] 1.5 mmol of triethylsilane was used.

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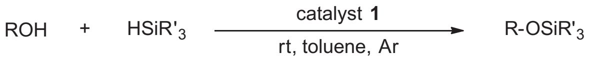
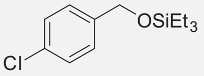
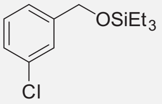
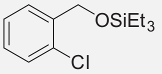
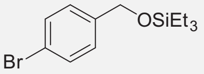
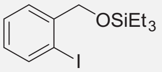
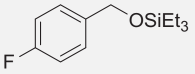
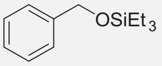
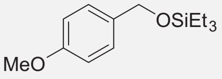
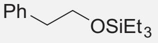
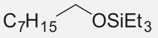
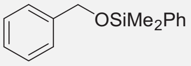
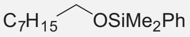
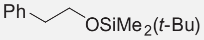
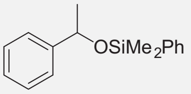
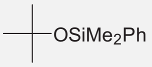
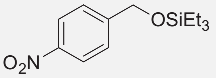
Here, we report the silylation of alcohols without additives under mild conditions using hydrosilanes and a recyclable ruthenium catalyst ($Ru/AlO(OH)$ (**1**)). Notably, C–X bonds of haloaryl groups survive under the conditions of the silylation,[13] which are generally labile toward oxidative addition in transition metal-catalyzed reactions. The ruthenium catalyst **1** is composed of ruthenium nanoparticles entrapped in aluminum oxyhydroxide, and can be easily prepared from readily available reagents through a simple sol–gel process.[14a] We have shown its high activity in the dehydrogenation of alcohols and in the synthesis of $\alpha,\beta$-unsaturated esters through one-pot alcohol oxidation–Wittig reaction.[14]

The characteristic activity of **1** was observed in the silylation of 4-chlorobenzyl alcohol with triethylsilane (Table 1). Although commercial Pd catalysts showed high activities in silylation, dechlorinated products were competitively formed in substantial amounts (entries 1 and 2). Commercial Ru catalysts showed chemoselectivities for the silylation, but the activities were much lower than that of **1** (entries 3 and 4). The silylation using **1** was tested in various solvents such as toluene, hexane, diethyl ether, and dichloromethane (entries 5–8). Toluene was the best among the solvents tested; (4-chlorobenzyloxy)triethylsilane was obtained selectively in 91% yield using 3.0 mol % of Ru after 24 h at room temperature under an argon atmosphere. The activity of **1** in hexane was comparable with that in toluene, while those in diethyl ether and dichloromethane were significantly lower.

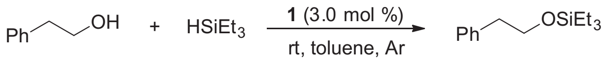
**Table 2**
Silylation of various alcohols using **1**[a]



| Entry | Silane | Product | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $HSiEt_3$ |  | 24 | 91[c,d] |
| 2 | $HSiEt_3$ |  | 24 | 88[d,e] |
| 3 | $HSiEt_3$ |  | 24 | 87[d,e] |
| 4 | $HSiEt_3$ |  | 24 | 95[c,d] |
| 5 | $HSiEt_3$ |  | 24 | 87[d,e] |
| 6 | $HSiEt_3$ |  | 24 | 90[d,e] |
| 7 | $HSiEt_3$ |  | 24 | 87 |
| 8 | $HSiEt_3$ |  | 24 | 85 |
| 9 | $HSiEt_3$ |  | 24 | 95[c] |
| 10 | $HSiEt_3$ |  | 24 | 90 |
| 11 | $HSiMe_2Ph$ |  | 18 | 95[c] |
| 12 | $HSiMe_2Ph$ |  | 18 | 87 |
| 13 | $HSiMe_2(t\text{-}Bu)$ |  | 24 | Trace[c] |
| 14 | $HSiMe_2Ph$ |  | 24 | 30[c] |
| 15 | $HSiMe_2Ph$ |  | 24 | Trace[c] |
| 16 | $HSiEt_3$ |  | 24 | Trace[c] |

[a] The reaction was performed on 1.0 mmol of alcohol and 1.2 mmol of hydrosilane in 3.0 mL of dry toluene with **1** (3.0 mol % of Ru) at 25 °C under Ar atmosphere.
[b] Isolation yield.
[c] Determined by GC with an internal standard.
[d] Dehalogenated products were not observed.
[e] 5.0 mol % of Ru was used.

**Table 3**
Recycling test for **1**[a]



| Run | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Yield[b] (%) | 95 | 93 | 93 | 93 | 94 |

[a] The reaction mixture was filtered through a glass filter. The recovered catalyst was washed with acetone, dried under vacuum for 3 h, and reused.
[b] Determined by GC with an internal standard.

Various alcohols were subjected in the catalytic silylation under the conditions of the entry 5 of Table 1 (Table 2). The catalytic silylation was effective not only for C–Cl bonds but also for C–Br, C–I, and C–F bonds of haloaryl groups (entries 1–6). Aliphatic primary alcohols were also successfully silylated (entries 9, 10, and 12). The silylations with dimethylphenylsilane were faster that those with triethylsilane (entries 11 and 12). However, our catalyst system was not effective for the silylation using $t$-$BuMe_2SiH$ (entry 13). Meanwhile, a secondary alcohol, 1-phenylethanol, was silylated only in 30% after 24 h (entry 14). In a competitive reaction using benzyl alcohol, 1-phenylethanol, and dimethylphenylsilane in 1:1:1.2 ratio, a 78:22 mixture of (benzyloxy)dimethylphenylsilane and 1-(dimethylphenylsiloxy)-1-phenylethane was obtained. *tert*-Butanol and an electron-deficient benzyl alcohol, (4-nitrophenyl)methanol, were practically inert toward our catalyst system (entries 15 and 16).

We tested the recyclability of **1** in the silylation of 2-phenylethanol with triethylsilane. The solid catalyst was recovered by filtration. Even in the fifth run, the catalytic activity is almost the same as that in the first use (Table 3).

In conclusion, we have demonstrated the silylation of various primary alcohols with hydrosilanes and a recyclable ruthenium catalyst under mild conditions without additives. The catalyst system is effective for the silylation of alcohols having haloaryl groups, and the C–X bonds survive during the silylation.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.119.

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