Pergamon

Tetrahedron Letters, Vol. 35, No. 45, pp. 8413-8414, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01816-2

Mild and Practical Method for the Silylation of Alcohols Using Hydrosilanes and Disilanes Promoted by TBAF Catalyst

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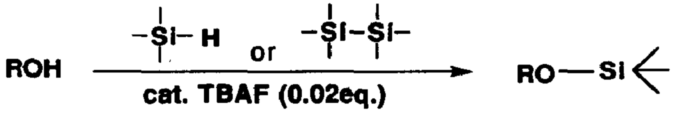
***Abstract*:** The primary and secondary alcohols were conveniently silylated (t-BuMe$_2$Si-, Et$_3$Si-, and Me$_2$PhSi-) using the hydrosilanes, and sterically hindered alcohols were also silylated (Me$_3$Si- and MePh$_2$Si-) using the disilanes, promoted by tetrabutylammonium fluoride (TBAF) catalyst under mild conditions.

The silylations of hydroxy groups have been well established as essential processes in the various fields of chemistry, especially as the most reliable protective methods in organic syntheses. It has been reported that alcohols are silylated using hydrosilanes catalyzed by transition metal complexes,[1] or by fluoride anion which is Corriu's pioneering finding as the activation method for the silicone-hydrogen bond.[2] The reactivity of the systems is, however, often unsatisfactory for synthetic purposes, especially in the case of synthetically useful t-butyldimethylsilyl (TBDMS) and triethylsilyl (TES) groups. Recently, we reported a nearly neutral and effective method for silylation by silazanes/catalytic tetrabutylammonium fluoride (TBAF) systems.[3] Here, we wish to describe an another facile silylation method for alcohols using hydrosilanes and disilanes/catalytic TBAF (0.02equiv.) system. served as an effective and convenient method for the silylation of alcohols. The process would be useful since the reaction conditions are essentially neutral and hydrogen gas is virtually the sole by-product which is ideal for practical, industrial, and ecological uses.[4]



$$\mathrm{ROH} \xrightarrow[\text{cat. TBAF (0.02eq.)}]{-\mathrm{Si}-\mathrm{H}\ \text{or}\ -\mathrm{Si}-\mathrm{Si}-} \mathrm{RO}-\mathrm{Si}\langle$$

Initially, triethylsilylation of 1-octanol with Et$_3$SiH in the presence of TBAF (0.02 equiv.) was examined in several solvents, and N-methylpyrolidone (NMP) was found superior to DMF or HMPA[2,5] while toluene and dimethoxyethane required refluxing conditions to proceed. Compared with the known RhCl(PPh$_3$)$_3$ (0.02 equiv.) and Pd(PPh$_3$)$_4$ (0.02 equiv.) catalyzed triethylsilylations, the present reaction proceeded faster in NMP at rt; T$_{1/2}$ s of conversion are 15-20 min/TBAF, about 1.5 h/RhCl(PPh$_3$)$_3$, and 4-5 h/Pd(PPh$_3$)$_4$. Results of the silylation of various types of alcohols using hydrosilanes and disilanes are listed in Table 1. Notable features of the new method are: (1) The reaction conditions are essentially neutral and the operation requires no special technique. (2) It is capable of introducing TBDMS and TES groups using corresponding hydrosilanes which are commercially available t-BuMe$_2$SiH and Et$_3$SiH. (3) Compared with the metal catalyzed reactions, hydrosilylation and/or hydrogenation of double or triple bonds in both substrates and allyldimethylsilane are completely suppressed. (4) Silylation of 1-octanol is predominant over the competitive reduction of 2-octanone when comparing the reactivity with the known ketone reduction of the hydrosilane/cat.TBAF system in HMPA[5] as exemplified by the experiment of hydrosilanes *vs.* an equimolar mixture of 1-octanol and 2-

octanone.[6] (5) Disilanes are found more reactive than the hydrosilanes. Accordingly, they were effective for the silylation of sterically crowded alcohols such as linalool and terpinen-4-ol. A slight excess of hydrosilanes (~1.5 equiv.) and more than 1 equiv. of disilanes were required for the sure completion of the reactions to compensate for the side formation of disiloxanes which would be produced by the reaction with oxygen dissolved in the solvent.

Table 1. Silylation of Alcohols Using Hydrosilanes and Disilanes by cat. TBAF[a)]

Entry	Alcohol	Silane[b)]	Temp.	Time (min)	GC-conv.(%)	Isolated yield (%)
1	1-Octanol	A	rt	30	100	---
2	1-Octanol	B	0~5°C	30	98	---
3	1-Octanol	C	0~5°C	30	98	---
4	1-Octanol	D[c)]	0~5°C	60	---	70
5	2-Octanol	A	rt	60	100	---
6	Benzyl alcohol	B	0~5°C	60	96	---
7	Geraniol	A	rt	60	99	95
8	Geraniol	B	0~5°C	60	97	95
9	Epoxide of citronellol	A	rt	60	99	97
10	Ethyl lactate	B[d)]	0~5°C	30	---	85
11	Cinnamyl alcohol	B	0~5°C	120	99	---
12	3-Butyn-1-ol	B	0~5°C	60	99	---
13	Epoxide of citronellol	E	rt	120	---	84
14	Linalool	E	rt	45	---	78
15	Linalool	F	rt	15	---	82
16	Terpinen-4-ol	E	rt	30	---	89
17	Terpinen-4-ol	F	rt	30	---	60

a) Molar ratio of Alcohol:Hydrosilane(Disilane):cat.TBAF=1.0:1.5(1.0):0.02. b) A:*t*-BuMe$_2$SiH, B:Et$_3$SiH, C:Me$_2$PhSiH, D:Allyl(Me)$_2$SiH, E:Me$_3$SiSiMe$_3$, F:MePh$_2$SiSiMePh$_2$. c) 3.0 equiv. of D was used in dimethoxyethane (solvent). d) 2.0 equiv. of B was used.

A typical procedure (Entry 7) is as follows: To a dried and degassed NMP solution (2 ml) of geraniol (1.00 mmol) and a THF solution of TBAF (1M solution, 20 μ l, 0.02 mmol) was added *t*-BuMe$_2$SiH (1.50 mmol) at rt which was then stirred at that temperature for 60 min under an argon atmosphere. Water was added and the usual work up followed by SiO$_2$ column chromatographic purification (hexane/ether = 300:1) which gave the TBDMS ether of geraniol in 95% yield.

This silyl-transfer reaction mechanism is considered to be similar to that of the previously reported silazanes.[3] The present silylation reaction would be applicable to practical or industrial uses. Further investigation on the TBAF catalyzed silyl-transfer reactions is under progress.

Acknowledgment: We thank Shin-etsu Chemical Co., Ltd. for the generous gift of *t*-butyldimethylsilane.

References and Notes

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2. Corriu, R. J. P. *Pure Appl. Chem.* **1988**, *60*, 99.
3. Tanabe, Y.; Murakami, M.; Kitaichi, K.; Yoshida, Y. *Tetrahedron Lett.* **1994**, *35*, in press.
4. In addition, widely used chlorosilanes such as chloro *t*-butyldimethylsilane are produced from the corresponding hydrosilanes in recent industrial process, so that these hydrosilanes are more economical products.
5. Fujita, M.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 5405.
6. The reaction was carried out in NMP at 0~5°C. These products ratios of 1-(trimethylsiloxy)octane: 2-(trimethylsiloxy)octane were as follows: 97:3 (Et$_3$SiH) and 84:16 (^{t}BuMe$_2$SiH).

(*Received in Japan* 16 *June* 1994; *accepted* 31 *August* 1994)