Base Promoted Preparation of Alkenylsilanols from Allylsilanes

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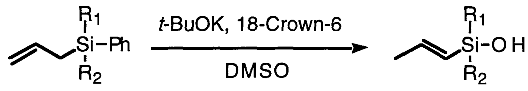
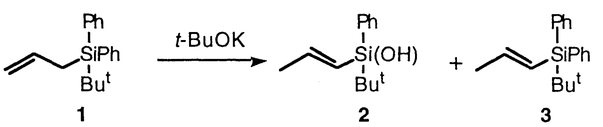
On treatment of allyl-*t*-butyldiphenylsilane with *t*-BuOK and 18-Crown-6 in DMSO at room temperature, isomerization of the olefinic double bond and subsequent substitution of phenyl group with hydroxy group took place smoothly to afford alkenylsilanol derivatives in good yields.

Temporary silicon connection pioneered by Stork[1] achieved the regiospecific, and often stereoselective, formation of carbon-carbon bonds by temporarily bringing together two reaction partners by means of an eventually removable silicon atom. The silicon tethered reaction has been established as an efficient method for the stereoselective construction of ring systems by numerous types of reactions such as ionic, radical, photochemical, and cycloaddition process.[2] Alkenylsilanol is thus considered to be a useful synthetic unit for the silyl tethered reactions. Furthermore, alkenylsilanols have been utilized as sila-analog of Sharpless asymmetric epoxidation[3] as well as of Simmons-Smith reactions.[4] It has, however, attracted little attention of synthetic organic chemists partly due to the lack of its excellent synthetic method.[5] We wish to disclose herein a simple base catalyzed protocol for the preparation of alkenylsilanols from readily available allylsilanes.



Scheme 1.

At the outset, on treatment of allyl-*t*-butyldiphenylsilane(**1**) with 1.5 equiv of *t*-BuOK in tetrahydrofuran, isomerization of the double bond took place smoothly at room temperature for 120 min to afford the corresponding alkenylsilane (**3**) in 82% yield (Entry 1, Table 1). The isomerization of **1** was complete in 15 min at room temperature in DMF to give **3** in 90% yield. In marked contrast, use of DMSO as a solvent completely changed the reaction course to give a vinylsilanol derivative (**2**) in 80% yield. Addition of 18-Crown-6 improved the yield of **2** to 89% (Entry 4).[6] Other bases were less satisfactory.[7] It is noted treatment of **3** with *t*-BuOK (2.0 equiv) in the presence of 18-Crown-6 (0.4 equiv) in DMSO at room temperature for 15 min gave rise to **2** in 84% yield.



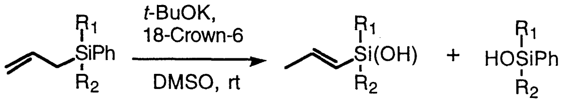
1 **2** **3**

Table 1. Effect of the solvent

Entry	Sovent	Yield /% 2	3
1	THF	0	82
2	DMF	0	90
3	DMSO	80	0
4	DMSO[a)]	89	0

a) 0.36 equiv of 18-Crown-6 was added.

Next, effect of the silyl substituent was studied and the results are shown in Table 2. Allylsilanes bearing sterically demanding silyl group gave corresponding alkenylsilanols in good yields. Allyltriphenylsilane gave **4** in 71% yield when the reaction was carried out initially at –45 °C and gradually warmed to room temperature (Entry 3). Formation of a silanol (**5**) was suppressed by carrying out the reaction at lower temperature. In the case of allyldimethylphenylsilane, the major product was a disiloxane, formed by dehydration of dimethylphenylsilanol (Entry 4). Among the silyl groups examined, *t*-butyldiphenylsilyl group exerted the best results (Entry 1).



4 **5**

Table 2. Effect of the silyl Group

Entry	R^1	R^2	Yield /% 4	5
1	*t*-Bu	Ph	89	10
2	*i*-Pr	*i*-Pr	52	29
3	Ph	Ph	71[a]	19
4	Me	Me	0	44[a,b]

a) The reaction was started initially at -45 °C in a mixture of DMSO and THF (v:v=1:4) and warmed to rt.
b) Isolated as a disiloxane produced by dehydration of the silanol.

The results of other *t*-butyldiphenylsilyl substituted allylsilanes are shown in Table 3. Transformation of

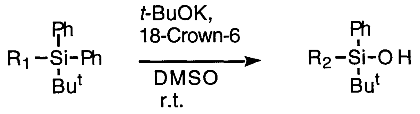
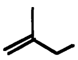
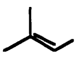
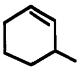
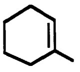


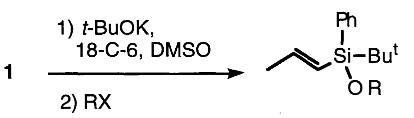
Table 3.

Entry	R_1	R_2	Yield / %
1			89
2			67
3			97[a]

a) The reaction was carried out at 50 °C for 20 min.

methallylsilane to the corresponding alkenylsilanol took place smoothly at room temperature in 67% yield (Entry 2). Although the present transformation generally proceeded smoothly at room temperature, 3-silylcyclohexene required heating at 50 °C for 20 min (Entry 3).

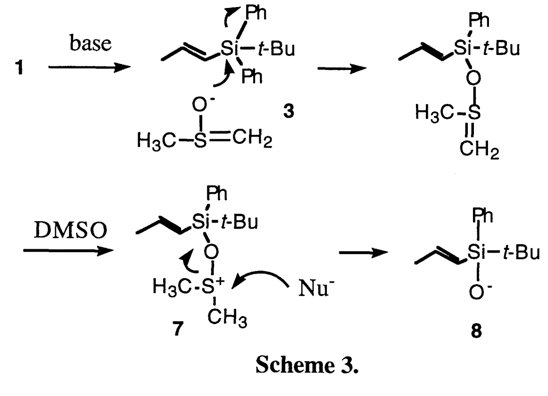
It is noted that when present reaction was quenched by addition of alkyl halide, such as methyl iodide and allyl bromide, corresponding silyl ethers (**6**) were obtained in one-pot reaction from the allylsilane in high yields as shown in Scheme 2.



6a; R=CH_3 77%
6b; R=$CH_2CH{=}CH_2$ 81%

Scheme 2.

The combination of KO-*t*-Bu in DMSO is used in cleavage of carbon-silicon bond.[8,9] Present transformation was found to proceed via initial isomerization of the olefinic double bond followed by substitution of the phenyl group with hydroxy moiety. In DMF, only isomerization of the double bond took place to furnish the corresponding alkenylsilane in a high yield. DMSO is hence requisite for the present transformation. Use of $(CD_3)_2SO$ as a solvent led to the incorporation of deuterium at both α and γ position of the silyl group of the alkenylsilanol (**2**). The fact that treatment of alkyl halide furnished the corresponding *O*-alkyl ethers (**6**) in good yields means that silanolate anion should be formed during the reaction. Participation of dimsyl anion, generated from DMSO, in the silanol formation is suggested. A plausible mechanism is shown in Scheme 3. Initially base catalyzed isomerization of the olefinic double bond took place[10] smoothly to furnish alkenylsilane (**3**). Dimsyl anion attacked the silicon atom followed by proton abstraction from DMSO to give a sulfonium salt (**7**). Nucleophilic attack of some nucleophile, supposedly either DMSO or dimsyl anion, to **7** afforded silanolate intermediate (**8**). When allylsilane bearing less bulky silyl substituent was employed, dimsyl anion attacked silyl moiety of **1** preferentially, leading to the elimination of allyl group to form *t*-butyldiphenylsilanol.



Scheme 3.

In conclusion, we have found a simple method for the preparation of alkenylsilanol from allylsilane by use of *t*-BuOK in DMSO.

References and Notes

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6 A typical experimental procedure for the preparation of (*E*)-propenyl-*t*-butylphenylsilanol (**2**) is described (Entry 4, Table 1). A solution of allyl-*t*-butyldiphenylsilane (**1**) (49.0 mg, 0.17 mmol) in DMSO (0.5 ml) and 18-crown-6 (16.6 mg, 0.06 mmol) were successively added to potassium *t*-butoxide (35.3 mg, 0.31 mmol) at room temperature. After being stirred at that temperature for 15 min, the reaction was quenched by addition of 1 mol dm^{-3} HCl solution. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2, hexane: ethyl acetate = 7:1, v/v) gave a mixture of (*E*)-propenyl-*t*-butylphenylsilanol (**2**) and *t*-butyldiphenylsilanol. ^{1}H NMR analysis of the mixture showed that **2** was obtained in 89% yield(*E*/*Z* = 97:3).
7 Yield of **2** utilizing other bases are as follows: KH; 67%, NaH; 12%, *n*-BuLi; 0%. When *n*-BuLi was employed as a base in DMSO, **3** was obtained in 80% yield.
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