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# Notes

## Conversion of Hydrosilanes to Silanols and Silyl Esters Catalyzed by $[Ph_3PCuH]_6$

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### Introduction

The most common preparative reactions for the conversion of Si−H groups to Si−OH groups are oxidations (for example, by $O_2$, $O_3$, $PhCO_3H$, $AgNO_3$, $AgNO_2$, dioxiranes, or $KMnO_4$) and hydrolyses.[1] Hydrolysis reactions[2,3] require acidic or basic conditions, which also promote the condensation of the formed silanols.

An interesting possibility is the use of metal catalysts for the conversion of Si−H into Si−OH or Si−O−Si groups. In some cases, this reaction accompanies the metal-catalyzed dehydrogenative coupling of hydrosilanes to oligo- or polysilanes.[4] However, there are also a few complexes which only catalyze the former reaction. The outcome of the metal-catalyzed reaction of hydrosilanes with water appears to depend to a high degree on the type of catalyst. For example, reaction of $Ph_2SiH_2$ with water in the presence of $Cp_2TiCl_2/Li^nBu$ as the catalyst quantitatively gave the disiloxane $Ph_2HSiOSiHPh_2$,[5] while in the presence of $(\pi\text{-}C_6H_6)(CO)_2Cr(\eta^2\text{-}H_2SiPh_2)$ a mixture of $Ph_2(HO)SiOSi(OH)Ph_2$, $Ph_2Si(OH)_2$, and siloxane oligomers was formed.[6] With the supported catalyst $Rh(CO)Cl[PPh_2CH_2CH_2SiO_{3/2}]_2{\cdot}x SiO_2$, prepared by sol−gel processing of $Rh(CO)Cl[PPh_2CH_2CH_2Si(OEt)_3]_2/Si(OEt)_4$ mixtures, only $Ph_2Si(OH)_2$ was obtained.[7]

An interesting aspect in the catalytic formation of Si−OH or Si−O−Si linkages from Si−H groups is the possibility to prepare sol−gel materials from hydrosilanes as an alternative to the usually employed alkoxysilanes. This was, *inter alia*, demonstrated for $H_3Si{-}C_6H_4{-}SiH_3$.[8]

We have previously shown that $[Ph_3PCuH]_6$ is a very active and highly selective catalyst for silane alcoholysis. It dehydrogenatively couples even tertiary alcohols with tertiary silanes and also with the least reactive triethylsilane under mild conditions. Furthermore, catalytic alcohol O-silylation occurs in the presence of competing C═C and C≡C bonds without hydrogenation or hydrosilylation.[9] In this paper, we report the extension of these studies to the reaction of hydrosilanes with water and carboxylic acids.

### Results and Discussion

The reactivity of hydrosilanes in alcoholysis and related reactions drops in the series $H_3SiR > H_2SiR_2 > HSiR_3$.[9,10] It can be assumed that a catalyst coupling tertiary silanes will be even more reactive with secondary and primary silanes. To probe the activity of $[Ph_3PCuH]_6$, we therefore only used tertiary silanes $R_3SiH$ with different substituents in the present study. They additionally have the advantage that only two types of products, $R_3SiOH$ or $R_3SiOSiR_3$, can be formed, but no oligomers or polymers.

When $Ph_3SiH$, $Ph_2MeSiH$, $PhMe_2SiH$, or $Et_3SiH$ was added to a THF solution of an equimolar amount of water and a catalytic amount (0.4 mol %) of $[Ph_3PCuH]_6$, the evolution of $H_2$ was observed. After a few hours at room temperature, the silanols $Ph_3SiOH$, $Ph_2MeSiOH$, or $Et_3SiOH$ were isolated in high yields (eq 1, Table 1), while the reaction with the more reactive $PhMe_2SiH$ gave the disiloxane $(PhMe_2Si)_2O$ (eq 2). The reactions were performed in the presence of air, because in the previously performed alcoholysis reactions the copper catalyst was much more active in air than under argon.[9]

$$R_3SiH + H_2O \xrightarrow{[Ph_3PCuH]_6} R_3SiOH + H_2 \qquad (1)$$

$$R_3Si = Ph_3Si,\ Ph_2MeSi,\ Et_3Si$$

$$2PhMe_2SiH + H_2O \xrightarrow{[Ph_3PCuH]_6} (PhMe_2Si)_2O + 2\ H_2 \qquad (2)$$

The easy reaction of the tertiary silanes with alcohols or water in the presence of $[Ph_3PCuH]_6$ as the catalyst prompted us to investigate the dehydrogenative coupling with other X−H bonds. While there was no reaction with $Et_2NH$, there was a quick reaction with acetic acid in benzene solution (eq 3, Table 1). The silyl acetates were formed in each case in good yields.

$$R_3SiH + CH_3COOH \xrightarrow{[Ph_3PCuH]_6} R_3SiOC(O)CH_3 + H_2 \qquad (3)$$

$$R_3Si = Ph_3Si,\ Ph_2MeSi,\ PhMe_2Si,\ Et_3Si$$

The use of $[Ph_3PCuH]_6$ as an efficient catalyst for the alcoholysis of hydrosilanes therefore can be extended to the reactions with water or carboxylic acids. Tertiary silanes, which are less prone to dehydrogenative coupling reactions than secondary or primary silanes, are readily converted under mild conditions to silanols (or siloxanes), or silyl carboxylates. There is no such reaction with amines, which probably deactivate the copper complex. The reactivity of the silanes decreases in the sequence $Ph_2MeSiH > Me_2PhSiH > Ph_3SiH > Et_3SiH$. About the same dependence on the type of the silane was found in the alcoholysis reactions.[9] The reactivity of the X−H compounds toward the tertiary silanes decreases in the order $CH_3COOH > H_2O > ROH$.

### Experimental Section

All operations were performed by standard Schlenk tube techniques in air. The solvents were dried and saturated with argon. Instrumentation: $^1H$ NMR spectra, Bruker AC 250; IR, Perkin-Elmer 1310. The hydrosilanes were prepared by standard procedures from the corre-

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**Table 1.** Reaction Times (at Room Temperature) and Isolated Yields for the Reaction of $Ph_3SiH$, $Ph_2MeSiH$, $Me_2PhSiH$, or $Et_3SiH$ with Water or Acetic Acid

| product | reaction time (h) | yield (%) | product | reaction time (h) | yield (%) |
|---|---|---|---|---|---|
| $Ph_3SiOH$ | 9 | 89 | $Ph_3SiOC(O)Me$ | 4 | 58 |
| $Ph_2MeSiOH$ | 6 | 87 | $Ph_2MeSiOC(O)Me$ | 1 | 66 |
| $(Me_2PhSi)_2O$ | 4 | 89 | $Me_2PhSiOC(O)Me$ | 1 | 67 |
| $Et_3SiOH$ | 9 | 50 | $Et_3SiOC(O)Me$ | 4 | 52 |

sponding chlorosilanes and $LiAlH_4$. $[Ph_3PCuH]_6$ was prepared by a literature procedure.[11]

**General Procedure for the Reaction of $R_3SiH$ with Water.** A 25.5 mmol (0.46 mL) aliquot of water was added to a solution of 200 mg (0.1 mmol) of $[Ph_3PCuH]_6$ in 10 mL of THF. Then 25.5 mol of the silane $R_3SiH$ was slowly added. There was vigorous evolution of $H_2$, and the color of the solution became yellow. The solution was then stirred for several hours (Table 1). The products were separated by distillation (except $Ph_3SiH$, which precipitated as a colorless solid) and characterized by $^1H$ NMR spectroscopy in comparison with literature data.[12]

$Ph_3SiOH$: mp 150 °C. $^1H$ NMR ($CDCl_3$, $\delta$): 4.38 (s, 1 H, OH). $Ph_2MeSiOH$: bp 94 °C ($10^{-2}$ Torr). $^1H$ NMR ($CDCl_3$, $\delta$): 4.05 (s, 1 H, OH), 0.92 (s, 3H, SiMe). $(PhMe_2Si)_2O$: bp 110 °C ($10^{-2}$ Torr). $^1H$ NMR ($CDCl_3$, $\delta$): 0.69 (s, 6 H, SiMe). $Et_3SiOH$: bp 61 °C ($10^{-2}$ Torr). $^1H$ NMR ($CDCl_3$, $\delta$): 4.47 (s, 1 H, OH), 0.99 (t, 9 H, CMe), 0.66 (q, 6 H, $CH_2$).

**General Procedure for the Reaction of $R_3SiH$ with Acetic Acid.** When 25.5 mmol of acetic acid was added to a solution of 200 mg (0.1 mmol) of $[Ph_3PCuH]_6$ in 10 mL of benzene, the solution turned immediately colorless. Then 25.5 mmol of the silane $R_3SiH$ was quickly added. There was vigorous evolution of $H_2$, and the color of the solution became yellow. The solution was then stirred for several hours (Table 1). The products were separated by distillation and characterized by $^1H$ NMR spectroscopy in comparison with the literature data.[13]

$Ph_3SiOC(O)Me$: bp 158 °C ($10^{-2}$ Torr). $^1H$ NMR ($CDCl_3$, $\delta$): 2.57 (s, 3 H, Me). $Ph_2MeSiOC(O)Me$: bp 99 °C ($10^{-2}$ Torr). $^1H$ NMR ($CDCl_3$, $\delta$): 2.56 (s, 3 H, CMe), 1.46 (s, 3 H, SiMe). $PhMe_2SiOC(O)Me$: bp 108 °C ($10^{-2}$ Torr). $^1H$ NMR ($CDCl_3$, $\delta$): 2.36 (s, 3 H, CMe), 0.93 (s, 6 H, SiMe). $Et_3SiOC(O)Me$: bp 80 °C ($10^{-2}$ Torr). $^1H$ NMR ($CDCl_3$, $\delta$): 2.22 (s, 3 H, CMe), 1.03 (t, 9 H, CMe), 0.65 (q, 6 H, $CH_2$).

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