An Efficient Catalyst for the Conversion of Hydrosilanes to Alkoxysilanes

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The copper(I) hydride $[Ph_3PCuH]_6$ is an efficient catalyst for the alcoholysis of primary and secondary silanes. The reactions proceed at room temperature within a few hours and give the alkoxysilanes in high yields. Only with bulky alcohols or silanes are longer reaction times and/or increased temperatures required. The presence of air accelerates the reactions and gives rise to higher yields of alkoxysilanes, particularly with bulky alcohols. Diols react with $PhRSiH_2$ (R = Me, Ph) to afford 1,3-dioxo-2-silacycloalkanes and with tertiary silanes to furnish the bissilylated diols. When unsaturated alcohols (2-propen-1-ol or 2-propyn-1-ol) are employed, the double or triple bond is retained.

Introduction

Alkoxysilanes are widely applied both in organic and inorganic chemistry, e.g. as protective groups in organic synthesis and in sol-gel preparations. They are usually prepared by reaction of chlorosilanes with either alcohols or alkoxides. Since these reactions either involve acidic (evolution of HCl) or basic conditions (alkoxide, or base as a HCl acceptor), alternative methods are sometimes advantageous. A particulary mild method is the alcoholysis of hydrogen-substituted silanes, because only H_2 is formed as a by-product. However, alcohols normally do not attack silanes in the absence of a catalyst, and most silanes undergo alcoholysis only in the presence of either strongly nucleophilic or electrophilic catalysts. Only a limited number of transition-metal complexes have been reported as homogeneous catalysts for the alcoholysis of hydrosilanes[1-11] (eq. 1).

$$x\,R'OH + R_{4-x}SiH_x \rightarrow R_{4-x}Si(OR')_x + x\,H_2 \qquad (1)$$

Only few of them can be used efficiently at room temperature[4-7] and most are not active with trialkylsilanes[1]. For instance, among the more active catalysts the Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, only dehydrocondenses Et_3SiH and alcohols in refluxing benzene[8-11], and Cp_2TiCl_2/*n*-BuLi[12] only transforms di- and trihydrosilanes into alkoxysilanes. The more reactive catalysts $Co_2(CO)_8$[4], $[IrCl(C_8H_{14})_2]_2$[5], and *cis*-$PtCl_2(PhC{=}CH_2)_2$[13] all catalyze alkene hydrosilation or hydrogenation, and therefore unsaturated alcohols cannot be employed. Crabtree's catalyst, $[IrH_2(THF)_2(PPh_3)_3]SbF_4$[7] does not show these problems, but rates are modest, and the activity declines drastically with the elongation and branching of the alkyl group in the alcohol.

We now report that the readily available copper hydride complex $[Ph_3PCuH]_6$[14] is a very reactive catalyst for the alcoholysis of hydrosilanes under mild reaction conditions. It provides silyl ethers in generally high yields and also with unsaturated alcohols.

Results and Discussion

The reactions of selected secondary and tertiary silanes with representative monofunctional alcohols (methanol, ethanol, isopropanol, *tert*-butanol) and phenol in the presence of $[Ph_3PCuH]_6$ are summarized in Table 1.

When the silane was added to a mixture of $[Ph_3PCuH]_6$ (0.4 mol-%) and an alcohol in benzene at room temperature, vigorous evolution of hydrogen occurred. The reactions in the presence of air were much faster than under argon. The rate of the alcoholysis depends on the type of the silane. Tertiary silanes containing at least one phenyl substituent reacted with methanol and ethanol in less than 1 h at room temperature. Reactions with isopropanol, *tert*-butyl alcohol and phenol also gave good conversions of the starting silane but required longer reaction times and/or heating to 40 °C. Although the rate of the reaction of triethylsilane with alcohols was the lowest, the isolated yields (between 80 and 90%) were comparable to those of the reactions of aryl-substituted silanes. Under argon the reactions with Et_3SiH did not go to completion after 48 h. The reactivity decreases in the sequence

$$Me_2PhSiH > Ph_2MeSiH > Ph_3SiH > Et_3SiH\,.$$

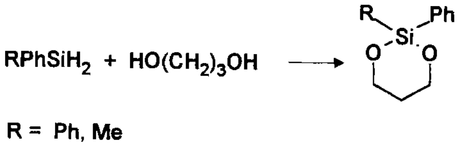
A study of the effect of the kind of the alcohol on the reactivity showed, as expected, that primary alcohols are most reactive, and secondary alcohols react faster than tertiary ones. It is worth noting that alcoholysis proceeds with sufficient yields and reaction rates even if both the alcohol (for instance *t*BuOH) and the silane (for instance Et_3SiH) are not very reactive. The observation that EtOH is more reactive than MeOH is unexpected and unprecedented, since all known catalysts show the greatest activity towards methanol.

The reaction rates decrease both in the absence and in the presence of air in the order

$$EtOH > MeOH > iPrOH > tBuOH \approx PhOH\,.$$

Secondary silanes reacted with alcohols by conversion of both Si–H bonds to Si–OR groups to afford overall yields ranging from 50 to 88% (Table 1). In addition, there was a residue upon distillation which shows only aromatic and aliphatic resonances in the ^{1}H-NMR spectrum indicative of polysiloxanes. Ph_2SiH_2 was more reactive than $PhMeSiH_2$; the reactivity of the alcohols decreased in the same order as for the tertiary silanes.

Reactions of equimolar amounts of tertiary silanes with diols yielded the bissilylated diols as expected; only the reaction of



(2)

Table 1. Reaction times, isolated yields and ^{1}H-NMR-spectroscopic data ($CDCl_3$) for the alkoxysilanes

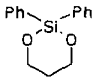
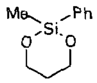
Alkoxysilane	Reaction Time (h)^A	Isolated Yields (%)^A	^{1}H-NMR ($CDCl_3$)(δ)^B
Ph_3SiOMe	5.5 (24)	80 (82)	3.65 (s, 3 H, CH_3)
$Ph_2MeSiOMe$	4 (7)	75 (60)	0.69 (s, 6 H, CH_3) 3.59 (s, 3 H, CH_3)
$Me_2PhSiOMe$	0.5-0.75 (1)	51 (75)	0.53 (s, 6 H, CH_3) 3.57 (s, 3 H, CH_3)
Et_3SiOMe	24 (^{D})	73 (40)	0.60 (q, 6 H, CH_2) 0.95 (t, 9 H, CH_3) 3.44 (s, 3 H, CH_3)
Ph_3SiOEt	5 (24)	66 (60)	1.30 (t, 3 H, CH_3) 3.93 (q, 2 H,CH_2)
$Ph_2MeSiOEt$	2 (5)	70 (67)	0.67 (s, 3 H, CH_3) 1.21 (t, 3 H, CH_3) 3.79 (q, 2 H, CH_2)
$Me_2PhSiOEt$	0.75 (1)	48 (59)	0.57 (s, 6 H, CH_3) 1.37 (t,3 H, CH_3) 3.86 (q, 2 H, CH_2)
Et_3SiOEt	24 (^{D})	73 (39)	0.70 (q, 6 H, CH_2) 1.07 (t, 9 H, CH_3) 1.29 (t, 3 H, CH_3) 3.78 (q, 2 H, CH_2) 3.87 (q, 4 H, CH_2)
$Ph_3SiO\mathit{i}Pr$	6.5 (24)	74 (60)	1.24 (d, 6 H, CH_3) 4.24 (sept, 1 H, CH)
$Ph_2MeSiO\mathit{i}Pr$	2 (6)	72 (67)	0.67 (s, 3 H, CH_3) 1.18 (d, 6 H, CH_3) 4.14 (sept, 1 H, CH)
$Me_2PhSiO\mathit{i}Pr$	1.75 (24)	55 (59)	0.57 (s, 6 H, CH_3) 1.32 (d, 6 H, CH_3) 4.18 (sept, 1 H, CH)
$Et_3SiO\mathit{i}Pr$	24 (^{D})	70 (37)	0.72 (q, 6 H, CH_2) 1.12 (t, 9 H, CH_3) 1.30 (d, 6 H, CH_3) 3.79 (sept, 1 H, CH)
$Ph_3SiO\mathit{t}Bu^C$	24 (24)	40 (74)	1.18 (s, 9 H, CH_3)
$Ph_2MeSiO\mathit{t}Bu^C$	24 (24)	69 (63)	0.62 (s, 3 H, CH_3) 1.29 (s, 9 H, CH_3)
$Me_2PhSiO\mathit{t}Bu^C$	24 (24)	40 (55)	0.66 (s, 6 H, CH_3) 1.56 (s, 9 H, CH_3)
$Et_3SiO\mathit{t}Bu^C$	24 (^{D})	77 (30)	0.58 (q, 6 H, CH_2) 0.99 (t, 9 H, CH_3) 1.73 (s, 9 H, CH_3)
Ph_3SiOPh^C	24 (24)	50 (30)	6.87-7.78 (m, 20 H, Ph)
$Ph_2MeSiOPh^C$	24 (24)	70 (76)	0.77 (s, 3 H, CH_3)
$Me_2PhSiOPh^C$	24 (24)	68 (88)	0.75 (s, 6 H, CH_3)
Et_3SiOPh^C	24 (^{D})	83 (31)	0.92 (q, 6 H, CH_2) 1.31 (t, 9 H, CH_3)
$Ph_2Si(OMe)_2$	1.5	76	3.54 (s, 6 H, CH_3)
$PhMeSi(OMe)_2$	4.5	83	0.47 (s, 3 H, CH_3) 3.66 (s, 6 H, CH_3)
$Ph_2Si(OEt)_2$	2.5	64	1.24 (t, 6 H, CH_3) 3.87 (q, 4 H, CH_2)
$PhMeSi(OEt)_2$	3.5	88	0.47 (s, 3 H, CH_3) 1.32 (t, 3 H, CH_3) 3.94 (q, 2 H, CH_2)
$Ph_2Si(O\mathit{i}Pr)_2$	2.5	74	1.25 (d, 12 H, CH_3) 4.31 (h, 2 H, CH)
$PhMeSi(O\mathit{i}Pr)_2$	4.5	88	0.49 (s, 3 H, CH_3) 1.33 (d, 12 H, CH_3) 4.32 (sept, 2 H, CH)
$Ph_2Si(O\mathit{t}Bu)_2$	4	79	1.25 (s, 18 H, CH_3)
$PhMeSi(O\mathit{t}Bu)_2$	6	60	0.62 (s, 3 H, CH_3) 1.48 (s, 18 H, CH_3)
$Ph_2Si(OPh)_2$	3,5	78	7.01-7.24 (m, 10 H, Ph)
$PhMeSi(OPh)_2$	5	51	0.99 (s, 3 H, CH_3)
$Ph_3SiO(CH_2)_2OH$	5	96	3.02 (s, br, OH) 3.76 (t, 2 H, CH_2) 3.98 (t, 2 H, CH_2)
$Ph_2MeSiO(CH_2)_2OSiMePh_2$	5	93	1.00 (s, 6 H, CH_3) 4.20 (t, 4 H, CH_2)
$Me_2PhSiO(CH_2)_2OSiMe_2Ph$	5	95	0.59 (s, 12 H, CH_3) 3.88 (t, 4 H, CH_2)
$Et_3SiO(CH_2)_2OSiEt_3$	5	90	0.59 (q, 12 H, CH_2) 0.92 (t, 18 H, CH_3) 3.62 (t, 4 H, CH_2)
$Ph_3SiO(CH_2)_3OSiPh_3$	5	97	1.89 (m, 2 H, CH_2) 3.89 (t, 4 H, CH_2)
$Ph_2MeSiO(CH_2)_3OSiMePh_2$	5	93	0.90 (s, 6 H, CH_3) 2.11 (m, 2 H, CH_2) 4.15 (t, 4 H, CH_2)
$Me_2PhSiO(CH_2)_3OSiMe_2Ph$	5	97	0.59 (s, 12 H, CH_3) 1.97 (m, 2 H, CH_2) 3.94 (t, 4 H, CH_2)
$Et_3SiO(CH_2)_3OSiEt_3$	5	89	0.51 (q, 12 H, CH_2) 0.87 (t, 18 H, CH_3) 1.57 (m, 2 H, CH_2) 3.83 (t, 4 H, CH_2)
	5	85	1.83 (m, 2 H, CH_2) 3.92 (m, 4 H, CH_2)
	5	87	0.43 (s, 3 H, CH_3) 1.87 (m, 2 H, CH_2) 4.05 (m 4 H, CH_2)
$Ph_3SiO(CH_2)_5OSiPh_3$	5	95	1.83 (m, 2 H, CH_2) 1.97 (m, 4 H, CH_2) 4.24 (t, 4 H, CH_2)
$Ph_2MeSiO(CH_2)_5OSiMePh_2$	5	94	1.00 (s, 6 H, CH_3) 1.82 (m, 2 H, CH_2) 1.92 (m, 4 H, CH_2) 4.06 (t, 4H, CH_2)
$Me_2PhSiO(CH_2)_5OSiMe_2Ph$	5	97	0.61 (s, 12 H, CH_3) 1.62 (m, 2 H, CH_2) 1.76 (m, 4 H, CH_2) 3.82 (t, 4 H, CH_2)
$Et_3SiO(CH_2)_5OSiEt_3$	5	91	0.56 (q, 12 H, CH_2) 0.91 (t, 18 H, CH_3) 1.36 (m, 2 H, CH_2) 1.54 (m, 4 H, CH_2) 3.55 (t, 4 H, CH_2)
$H_2C{=}CHCH_2OSiPh_3$	4	95	4.47 (d, 2 H, CH_2) 5.22 (d, 1 H) 5.47 (d, 1 H) 6.06 (m, 1 H)
$H_2C{=}CHCH_2OSiPh_2Me$	4	92	0.99 (s, 3 H, CH_3) 4.57 (d, 2 H, CH_2) 5.42 (d, 1 H) 5.65 (d, 1 H) 6.26 (m, 1 H)
$H_2C{=}CHCH_2OSiMe_2Ph$	4	93	0.60 (s, 3 H, CH_3) 4.33 (d, 2 H, CH_2) 5.28 (d, 1H) 5.47 (d, 1 H) 6.11 (m, 1 H)

Table 1 *(Continued)*

Alkoxysilane	Reaction Time (h)[A]	Isolated Yields (%)[A]	^{1}H-NMR ($CDCl_3$)(δ)[B]
$H_2C{=}CHCH_2OSiEt_3$	4	84	0.64 (q, 6 H, CH_2) 0.96 (t, 9 H, CH_3) 4.17 (d, 2 H, CH_2) 5.07 (d, 1 H) 5.39 (d, 1 H) 6.25 (m, 1 H)
$HC{\equiv}CCH_2OSiPh_3$	4	67	2.52 (t, 1 H, CH) 4.64 (d, 2 H, CH_2)
$HC{\equiv}CCH_2OSiPh_2Me$	4	73	0.99 (s, 3 H, CH_3) 2.60 (t, 1 H, CH) 4.60 (d, 2 H, CH_2)
$HC{\equiv}CCH_2OSiMe_2Ph$	4	71	0.59 (q, 6 H, CH_2) 2.50 (t, 1 H, CH) 4.38 (d, 2 H, CH_2)
$HC{\equiv}CCH_2OSiEt_3$	4	65	0.65 (q, 6 H, CH_2) 0.97 (t, 9 H, CH_3) 2.45 (t, 1 H, CH) 4.27 (d, 2 H, CH_2)

[A] The values in brackets are the reaction times and yields, if the reactions are run under an atmosphere of argon instead of air. – [B] The phenyl resonances are omitted. They are observed in the usual range and with the correct intensity. – [C] 40 °C. – [D] Reaction did not go to completion within 48 h.

Ph_3SiH with 1,2-ethanediol resulted in the mono-silylated product (Table 1). The reaction of secondary silanes with 1,3-propanediol furnished 1,3-dioxo-2-silacyclohexane (eq 2).

The copper(I) hydride cluster is an efficient and convenient reagent for the regiospecific and stereoselective conjugate hydride reduction of α,β-unsaturated carbonyl compounds in high yields[15]. This reaction is general for α,β-unsaturated ketones and esters. The copper hydride hexamer is completely inert towards unactivated alkenes. Isolated double bonds, carbonyl goups, and a variety of oxygenated functionalities are not reduced. Therefore, a hydroxy group can be silylated by using this complex as catalyst when another reactive functional group is present in the same molecule. Silyl ethers were obtained by the reaction of 2-propen-1-ol and 2-propyn-1-ol with tertiary silanes without detectible formation of byproducts, resulting from the hydrosilylation or hydrogenation of the C=C andc C≡C bond (Table 1). In the case of 2-propyn-1-ol the reaction did not go to completion within 4 hours; a small amount of the starting silane was recovered and removed by distillation.

Conclusion

This study shows that $[Ph_3PCuH]_6$ is a very efficient and highly selective catalyst for the silane alcoholysis.

- The copper hydride cluster is easily accessible.
- This catalyst dehydrogenatively couples even tertiary alcohols with the less reactive triethylsilane under mild conditions.
- Catalytic alcohol *O*-silylation occurs in the presence of competing C=C and C≡C bonds without hydrogenation or hydrosilylation.

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Experimental

All reactions were performed by standard Schlenk tube techniques. – NMR: Bruker AC 250. – IR: Perkin-Elmer 1310. – The following compounds were prepared by standard procedures from the corresponding chlorosilanes and $LiAlH_4$: Me_2PhSiH[17], Et_3SiH[18], Ph_2SiH_2[19], $PhMeSiH_2$[19]. The alcohols were dried by distillation from sodium, or from magnesium in the case of methanol. $[Ph_3PCuH]_6$ was prepared by a literature procedure[14].

General Procedure for the Reaction of Silanes with Alcohols: The silane R_3SiH or R_2SiH_2 (25.5 mmol, or 51.0 mmol R_3SiH in the reaction with diols) was added to a benzene solution (10 ml) containing the alcohol R'OH (25.5 mmol) (or 51.0 mmol for the secondary silanes) and $[Ph_3PCuH]_6$ (0.102 mmol). Gas evolution from the red solution started immediately; reactions with MeOH were noticeably exothermic. When the reactions were performed in the presence of air, the Schlenk tube was opened to the atmosphere after silane addition. The reactions were monitored by IR; complete disappearence of the Si–H absorption showed the end of the reaction. Petroleum ether (boiling range 30–40 °C) was then added to the solution to precipitate the catalyst. Filtration, removal of the solvent and distillation or crystallization of the residue gave the alkoxysilanes. The products were characterized by ^{1}H NMR (Table 1). Their identity was established by their physical properties and spectroscopic data.

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[1] E. Lukevics, M. Dyintara, *J. Organomet. Chem.* **1985**, *295*, 265.
[2] N. J. Archer, R. N. Haszeldine, R. V. Parish, *J. Chem. Soc., Dalton Trans.* **1979**, 695.
[3] J. A. Davies, F. R. Hartley, S. G. Murray, G. Marshall, *J. Mol. Catal.* **1981**, *10*, 171.
[4] A. J. Chalk, *J. Chem. Soc., Chem. Commun.* **1970**, 847.
[5] S. N. Blackburn, R. N. Haszeldine, R. V. Parish, J. H. Setchfi, *J. Organomet. Chem.* **1980**, 329.
[6] U. Oehmichen, H. Singer, *J. Organomet. Chem.* **1983**, *243*, 199.
[7] X.-L. Luo, R. H. Crabtree, *J. Am. Chem. Soc.* **1989**, *111*, 2527.
[8] I. Ojima, T. Kogure, M. Nihonyanigi, H. Kono, S. Inaba, Y. Nagai, *Chem. Lett.* **1973**, 501.
[9] R. J. P. Corriu, J. J. E. Moreau, *J. Organomet. Chem.* **1977**, *127*, 7.
[10] R. J. P. Corriu, J. J. E. Moreau, *J. Organomet. Chem.* **1976**, *114*, 135.
[11] R. J. P. Corriu, J. J. E. Moreau, *J. Organomet. Chem.* **1976**, *120*, 337.
[12] T. C. Bedard, J. Y. Corey, *J. Organomet. Chem.* **1992**, *428*, 315.
[13] W. Caseri, P. S. Pregosin, *Organometallics* **1988**, *7*, 1373.
[14] D. M. Brestensky, D. E. Huseland, C. McGettigan, J. M. Stryker, *Tetrahedron Lett.* **1988**, *29*, 3749.
[15] U. S. Mahoney, D. M. Brestensky, J. M. Stryker, *J. Am. Chem. Soc.* **1988**, *110*, 291.
[16] R. West, E. G. Rochow, *J. Org. Chem.* **1953**, *18*, 303.
[17] S. Tannenbaum, *J. Am. Chem. Soc.* **1953**, *75*, 3753.
[18] M. C. Harvey, W. H. Nebergall, J. S. Peake, *J. Am. Chem. Soc.* **1954**, *79*, 4555.

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