

Preliminary communication

A novel route to silylthioethers

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Silylthioethers are normally prepared by reaction of a chlorosilane with a metal mercaptide^{1a} or by substitution of a silylamine with mercaptans^{1b}; many reports have been published concerning the properties and reactivities of these compounds¹. In contrast to Pd–C which does not catalyse the reaction between hydrosilanes and mercaptans², we wish to report that tris(triphenylphosphine)chlororhodium, an exceedingly active hydrogenation³ and hydrosilylation⁴ catalyst, catalyses the dehydrogenative condensation and thus provides a novel route to silylthioethers.

In a typical procedure, a mixture of 1.10 g (10 mmol) of thiophenol and 1.16 g (10 mmol) of triethylsilane and 50 mg (0.5 mol%) of tris(triphenylphosphine)chlororhodium was stirred and heated to 50° (bath temperature) for 15 min. After the vigorous evolution of hydrogen had subsided, the reaction mixture was poured into 50 ml of n-hexane and the precipitated catalyst was removed by filtration. The filtrate was concentrated and distillation of the residue under reduced pressure gave thiophenoxy(triethyl)silane (b.p. 77°/0.25 mm) in quantitative yield.

Results of the dehydrogenative condensation between various hydrosilanes and mercaptans are summarized in Table 1. Yields of the silylthioethers were almost quantitative in all cases as revealed by GLPC analyses.

The rate of reaction was found to be dependent upon the nature of the mercaptan and the hydrosilane. Thiophenol reacts distinctly faster than do alkylmercaptans which require heating for a rather prolonged period. The reactivity of benzylmercaptan is similar to that of thiophenol. A phenyl substituent on silicon increases the reactivity, thus phenyldimethylsilane reacts eight times faster than triethylsilane with thiophenol in benzene at room temperature*. Dihydrosilanes are much more reactive than monohydrosilanes

* Two hydrosilanes in equimolar amounts (5 equiv.) were allowed to compete for a deficiency of thiophenol (1 equiv.) at 27° for 2 h, and the reactivity ratio was determined on the basis of the relative amounts (GLPC) of silylthioether products.

TABLE 1

DEHYDROGENATIVE CONDENSATION OF HYDROSILANES WITH MERCAPTANS

$$\equiv\text{SiH} + \text{HSR} \xrightarrow{(\text{Ph}_3\text{P})_3\text{RhCl}} \equiv\text{Si-SR} + \text{H}_2$$

| Hydrosilane | Mercaptan | Quantity of catalyst. (Mol %) | Reaction conditions | Product ^a | B.p. (°C/mm) |
|----------------------------------|----------------------|-------------------------------|-------------------------|---------------------------------------|--------------|
| Me ₃ SiH | PhSH | 0.5 | 6°, 60 min ^b | Me ₃ SiSPh | 88/15 |
| Et ₃ SiH | PhSH | 0.5 | 50°, 15 min | Et ₃ SiSPh | 77/0.25 |
| n-Pr ₃ SiH | PhSH | 0.5 | 70°, 60 min | n-Pr ₃ SiSPh | 92/0.4 |
| PhMe ₂ SiH | PhSH | 0.5 | 50°, 5 min | PhMe ₂ SiSPh | 113/0.6 |
| Et ₃ SiH | EtSH | 0.5 | reflux, 240 min | Et ₃ SiSEt | 99/24 |
| Et ₃ SiH | t-BuSH | 0.5 | 70°, 240 min | Et ₃ SiS <i>t</i> -Bu | 108/21 |
| Et ₃ SiH | PhCH ₂ SH | 0.5 | 70°, 30 min | Et ₃ SiSCH ₂ Ph | 168/21 |
| Ph ₂ SiH ₂ | PhSH | 0.1 | r.t., 15 min | Ph ₂ HSiSPh | 151/0.2 |
| PhMeSiH ₂ | PhSH | 0.1 | r.t., 30 min | PhMeHSiSPh | 162/17 |
| Et ₂ SiH ₂ | PhSH | 0.1 | 15°, 30 min | Et ₂ HSiSPh | 131/23 |
| Ph ₂ SiH ₂ | EtSH | 0.1 | r.t., 30 min | Ph ₂ HSiSEt | 130/0.65 |
| PhMeSiH ₂ | EtSH | 0.1 | r.t., 30 min | PhMeHSiSEt | 107/17 |
| Et ₂ SiH ₂ | EtSH | 0.1 | r.t., 30 min | Et ₂ HSiSEt | 126/760 |

^a The NMR and IR spectra and elemental analyses of all new compounds were consistent with the assigned structures. ^b n-Hexane was used as a solvent.

giving monohydrosilylthioethers which are difficult to synthesize by usual methods¹. In this case, the reactivity order is: Et_2SiH_2 (1.0) < PhMeSiH_2 (1.4) < Ph_2SiH_2 (3.6) as indicated by competitive experiments.

The values of $J(^{29}\text{Si}-\text{H})$ for $\text{Ph}_2(\text{PhS})\text{SiH}$, $\text{PhMe}(\text{PhS})\text{SiH}$, $\text{Et}_2(\text{PhS})\text{SiH}$, $\text{Ph}_2(\text{EtS})\text{SiH}$, $\text{PhMe}(\text{EtS})\text{SiH}$, $\text{Et}_2(\text{EtS})\text{SiH}$, thus prepared, were determined as -222.8 , -217.1 , -205.4 , -216.7 , -210.8 and -200.4 Hz, respectively, on the basis of their NMR spectra. The large absolute values of $J(^{29}\text{Si}-\text{H})$ for these compounds, compared to that for triethylsilane, -179.6 Hz, may reflect the large fraction of *s* character employed by silicon in its bond to hydrogen⁵.

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