

Preliminary communication

A general route to five-coordinate hydridosilicates

B. Becker, R. Corriu *, C. Guerin, B. Henner and Q. Wang

*Laboratoire "Hétérochimie et Amino-Acides", U.A. CNRS 1097, Institut de Chimie Fine,
 Université des Sciences et Techniques du Languedoc, 34060 Montpellier cedex (France)*

(Received October 10th, 1988)

Abstract

Five-coordinate potassium hydridosilicates, $[\text{HSi}(\text{OR})_4]^- \text{K}^+$ ($\text{R} = \text{Et}, \text{i-Pr}, \text{Ph}$), have been obtained in good yield from the reaction of a trialkoxy- or triaryloxy-silane with the corresponding potassium alkoxide or aryloxide, and characterized spectroscopically. Reaction of the hydrosilicates with an excess of Grignard reagent gives the corresponding triorganosilanes.

Introduction

As a part of our systematic investigation of the reactions of hypervalent organo-silicon species [1], we became interested in pentacoordinate anionic hydridosilicates for two main reasons:

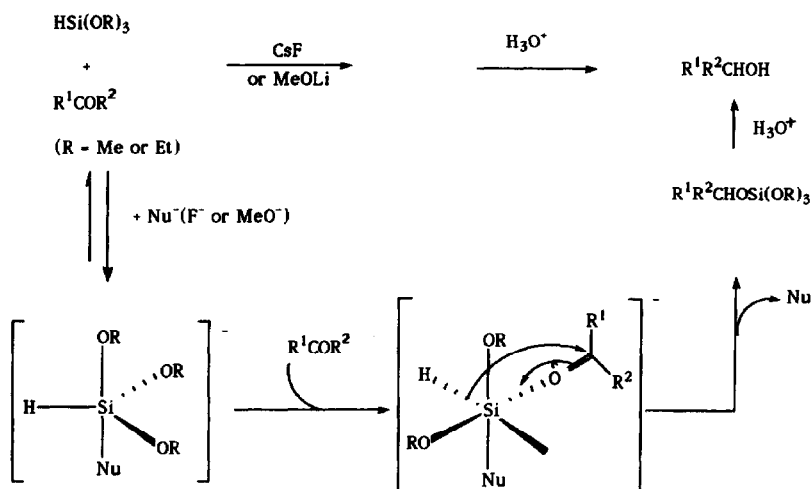
- (1) Numerous pentacoordinated silicon compounds have been reported [2] and their structures discussed [3], but no general synthetic route to hydridosilicates has been developed.
- (2) Pentacoordinated hydridosilicates have been suggested to be reactive intermediates in the reduction of aldehydes and ketones with hydrosilanes catalyzed by fluoride [4] or alkoxide [5] ions (Scheme 1).

We have now found that these pentacoordinated hydridosilicates may be obtained directly from the reaction of an alkoxy- or aryloxy-hydrosilane with the corresponding potassium alkoxide or aryloxide.

Treatment of triethoxysilane $\text{HSi}(\text{OEt})_3$ with one equivalent of potassium ethoxide as a suspension in a large excess of THF or DME at room temperature yielded the corresponding hydridosilicate 1 (eq. 1) which was isolated as a white powder by removal of the solvent.



($\text{R} = \text{Et}, \text{i-Pr}, \text{Ph}$) (1–3)(80–90%)



Scheme 1

This reaction, which is general for other potassium alkoxides or aryloxides, can be optimized to give yields of up to 80–90%. In sharp contrast, sodium or lithium alkoxides failed to give the hydridosilicates. The use of a crown-ether specific for potassium is not necessary to stabilize the products [6].

The hydridosilicates, 1–3 (eq. 1), gave satisfactory spectroscopic data. In particular, the ^{29}Si NMR chemical shifts were in the usual range for anionic pentacoordinated silicates [7]; as expected, upfield shifts of the ^{29}Si NMR resonances relative to those of the corresponding alkoxy- or aryloxy-silanes were observed. The ^{29}Si –H coupling constants are consistent with a five-coordinate structure [6]. The value of the ^1H – ^{29}Si coupling constant is smaller for the five-coordinated silicates than for the neutral corresponding species (Table 1), as expected from the decrease in the proportions of *s* character of the orbital of the Si–H bond.

As observed previously for *o*-arenediolato- and fluoro-organosilicates [1], 1 reacts readily with an excess of a Grignard reagent RMgBr , at low temperature; whatever the nature of the nucleophile ($\text{R} = \text{n-Bu}$, Ph or PhCH_2), the triorganosilane R_3SiH was obtained in high yield (eq. 2), and the formation of such compounds provides sound chemical evidence for the nature of compound 1.

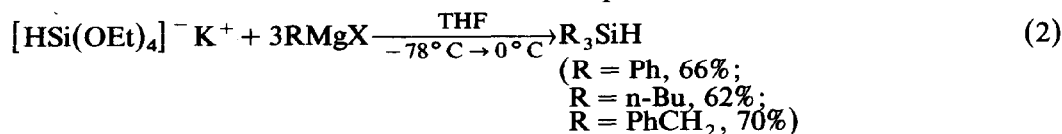


Table 1

^{29}Si NMR spectral data for 1–3 (S = THF)

HSi(OEt)_3	$\delta -58.8$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 285 Hz)
$[\text{HSi(OEt)}_4]^-$ 1	$\delta -88.1$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 223 Hz)
$\text{HSi(O-}i\text{-Pr)}_3$	$\delta -62.7$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 285 Hz)
$[\text{HSi(O-}i\text{-Pr)}_4]^-$ 2	$\delta -90.7$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 214 Hz)
HSi(OPh)_3	$\delta -70.5$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 320 Hz)
$[\text{HSi(OPh)}_4]^-$ 3	$\delta -111.9$ ppm (d, $J(^1\text{H}-^{29}\text{Si})$ 296 Hz)

It is evident that we devised a general method for the preparation of potassium hydridosilicates. These compounds should be excellent models for examining of the mechanism of reduction of carbonyl derivatives by hydrosilanes. Further studies aimed at elucidation of the special features of the reactions of these five-coordinate species are in progress.

References

- 1 R. Corriu, C. Guerin and J. Moreau, *Top. Stereochem.*, 15 (1984) 158; A. Boudin, G. Cerveau, C. Chuit, R. Corriu and C. Reye, *Angew. Chem. Int. Ed. Engl.*, 25 (1986) 473; J. Boyer, C. Breliere, R. Corriu, A. Kpoton, M. Poirier and G. Royo, *J. Organomet. Chem.*, 311 (1986) C39; R. Corriu, C. Guerin, B. Henner and W.W.C. Wong Chi Man, *Organometallics*, 7 (1988) 237; R. Corriu, 8th Intern. Organosilicon Symposium, Ellis Horwood Ltd, Chichester, England, 1988; P. Arya, J. Boyer, R. Corriu, G. Lanneau and M. Perrot, *J. Organomet. Chem.*, 346 (1988) C11; and ref. therein.
- 2 A. Weiss, A. Herzog in G. Bendz, I. Lindquist (Eds.), *Biochemistry of Silicon and Related Problems*, Plenum, New York, 1978, p. 109; St. N. Tandura, N.V. Alekseev and M.G. Voronkov, *Top. Curr. Chem.*, 131 (1986) 99.
- 3 For instance, R.R. Holmes, R.O. Day, J.J. Harland, A.C. Sau and J.M. Holmes, *Organometallics*, 3 (1984) 341; R.R. Holmes, R.O. Day, J.J. Harland and J.M. Holmes, *ibid.*, 3 (1984) 347; J.J. Harland, J.S. Payne, R.O. Day and R.R. Holmes, *Inorg. Chem.*, 26 (1987) 760.
- 4 J. Boyer, R. Corriu, R. Perz and C. Reye, *Tetrahedron*, 37 (1981) 2165; J. Boyer, R. Corriu, R. Perz, M. Poirier and C. Reye, *Synthesis*, (1981) 558; C. Chuit, R. Corriu, R. Perz and C. Reye, *ibid.*, (1982) 981.
- 5 M. Fujita, T. Hiyama, *J. Am. Chem. Soc.*, 106 (1984) 4629; A. Hosomi, H. Hayashida, S. Kohra and Y. Tominaga, *J. Chem. Soc. Chem. Commun.*, (1986) 1411; M. Kira, K. Sato and H. Sakurai, *J. Org. Chem.*, 52 (1987) 948.
- 6 R. Damrauer and S.E. Danahey, *Organometallics*, 5 (1986) 1490.
- 7 W.H. Stevenson III, S. Wilson, J.C. Martin and W.B. Farnham, *J. Am. Chem. Soc.*, 107 (1985) 6340; M. Kira, K. Sato and H. Sakurai, *Chem. Lett.*, (1987) 2243; C. Breliere, R. Corriu, M. Poirier and G. Royo, unpublished results.