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Preliminary communication

Pentavalent hydridosilicates: some aspects of the reactivity of potassium tetraethoxyhydridosilicate

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Abstract

Some reactions of the pentacoordinate tetraethoxyhydridosilicate, $[HSi(OEt)_4]^-$, are reported. The ready reduction of ketones and aldehydes in the absence of a catalyst indicates the high reactivity of the Si–H bond in this compound which also readily shows good one electron transfers to an appropriate substrate.

There is much interest in the known stable penta- and hexa-coordinate silicon derivatives, and their structures have attracted considerable attention [1]. The reactions [2], including isomerization processes [3], of these compounds are also of importance. As a part of our programme of investigations of the reactivity of hypervalent organosilicon species [4], our efforts have recently focused on pentacoordinate anionic hydridosilicates, and we recently described [5] a general route to potassium hydridosilicates, involving the reaction of an alkoxy- (or aryloxy-)hydrosilane with the corresponding potassium alkoxide (or aryloxide) (éq. 1).

$$HSi(OR)_3 + ROK \xrightarrow{\text{THF or DME}} [HSi(OR)_4]^- K^+ \qquad (1)$$

(R = Et, i-Pr, Ph)

We now report preliminary results on the reactivity of $[HSi(OEt)_4]^- K^+$ (**1**).

The isolated hydridosilicate **1** was found to be an effective reducing agent for the carbonyl compounds in the absence of a catalyst at room temperature. The results are listed in Table 1.

Yields of primary and secondary alcohols were generally excellent (up to 90%); the lower yield in the case of acetophenone could be attributed to partial enolisation of the starting material under the influence of ethoxide ions liberated during the

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Table 1

Reduction of carbonyl compounds

$$[\mathrm{H{-}Si(OEt)_4}]^- \mathrm{K}^+ + \mathrm{R^1COR^2} \xrightarrow[\substack{0\,^\circ\mathrm{C\ or\ r.t.} \\ (2)\ \mathrm{H_3O^+}}]{(1)\ \mathrm{THF}} \mathrm{R^1R^2CHOH}$$

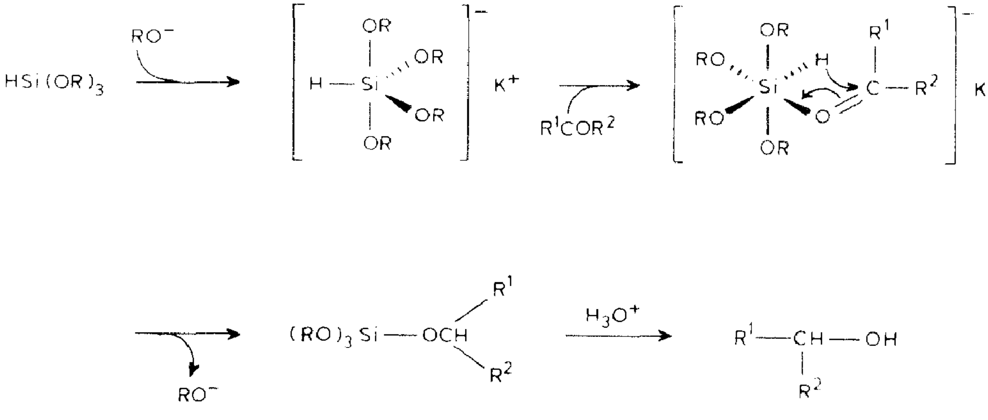
R^1	R^2	R^1R^2CHOH%
Ph	H	90
$CH_3(CH_2)_3$	H	80
Ph	Ph	73
Ph	CH_3	44

reaction. From the mechanistic point of view, these results clearly indicate that the reduction of carbonyl compounds by trialkoxysilanes catalysed by alkoxide or fluoride ions takes place by in-situ generated pentacoordinate hydrides related to **1** [6] (Scheme 1).

The reduction of benzophenone gave only benzhydrol; no trace of the blue colored ketyl radical anion was detected during the reaction, and no benzopinacol was recovered. This is indicative of a polar mechanism, such as that shown in Scheme 1.

The pentavalent anion formed in situ from the phenyldimethylsilane and fluoride anion has been reported previously to be a single electron transfer (SET) reagent [7], and so the reactions of **1** with organic halides were also investigated (Table 2).

The hydridosilicate **1** reacted smoothly with alkyl halides to give the corresponding alkanes in 30–40% yields after 2 days, the bromides being more reactive than the chlorides; concomitant formation of $Si(OEt)_4$ was observed. Reaction of **1** with one equivalent of $PhCH_2Br$ or Ph_2CHCl gave the reduced dimer as major product as well as the expected toluene and diphenylmethane respectively. These results suggest that the reaction may involve a single electron transfer from **1** to the substrate as an initial process. The reaction of **1** with 6-bromohexene, which serves as an indicator



Scheme 1

Table 2

Reduction of organic halides

$$[HSi(OEt)_4]^-K^+ + RX \xrightarrow[48\ h]{THF} RH + RR + Si(OEt)_4$$

X = Br, r.t.

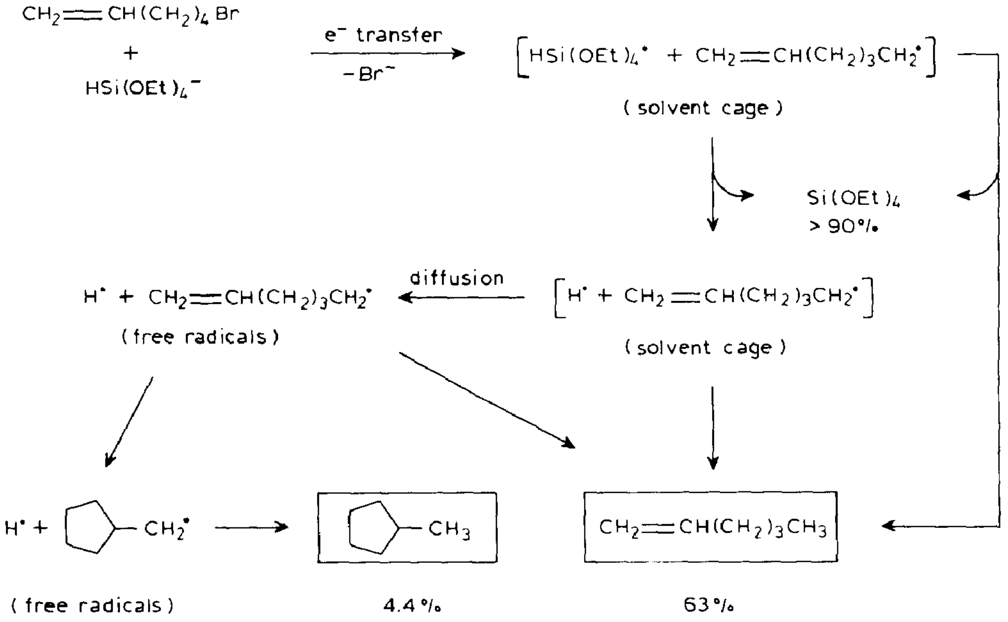
X = Cl, 45° C

R	X	RH	RR
$C_{12}H_{25}$	Cl	33	–
–	Br	47	–
$PhCH_2$	Br	20	30
Ph_2CH	Cl	12	40

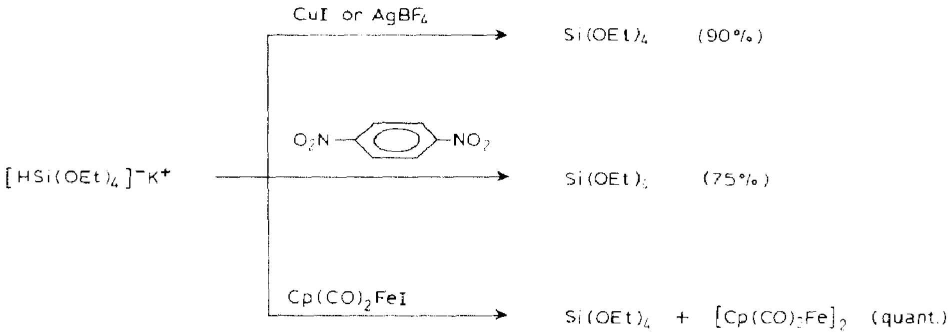
of SET processes in reactions of organic halides with nucleophiles [8], led only to a 4.4% yield of the rearranged cyclic product (Scheme 2).

To account for these results we suggest that in the solvent cage the radical $[HSi(OEt)_4]^{\cdot}$ generated from the initial electron-transfer step either acts as an efficient hydrogen-transfer agent or undergoes fast breakdown to $H^{\cdot}$ and $Si(OEt)_4$, as outlined in Scheme 2; as a consequence, the 5-hexenyl intermediate radical must be intercepted before it can cyclize to methylcyclopentane. At present we cannot completely exclude the operation of a one-stage nucleophilic mechanism in the case of alkyl halides.

The ability of the pentacoordinate hydridosilicate to transfer one electron was confirmed in reactions with species such as Cu^+ and Ag^+ cations, or $Cp(CO)_2FeI$. Furthermore a reaction mixture containing added *p*-dinitrobenzene (DNB) turned green, indicating the formation of the radical anion of DNB [9] (Scheme 3).



Scheme 2



Scheme 3

In all cases, $Si(OEt)_4$ is the major organosilicon product (up to 90% yield); in the case of the iron iodide complex, the reaction gave the iron dimer quantitatively.

The results can be summarized as follows:

(i) The pentavalent hydridosilicate $[HSi(OEt)_4]^- K^+$ shows high reactivity as a reducing agent towards carbonyl derivatives. The results indicate unambigously the intermediacy of such pentavalent compounds as active hydride species in the reduction of aldehydes or ketones with trialkoxysilanes catalyzed by fluoride or alkoxide ions.

(ii) The hydridosilicate **1** also acts as an electron donor towards organic halides and oxidizing species. The data suggest the operation of a single-electron-transfer process. Further work is in progress.

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