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Preliminary communication

$(Me_3Si)_3SiSH$: a new radical-based reducing agent

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Abstract

Tris(trimethylsilyl)silanethiol is an effective and useful reducing agent for some organic substrates. The reduction involves free-radical chain reactions.

In organic synthesis the most useful types of free radical reactions are (i) reductions of a variety of functional groups (eqs. 1 and 2 represent the propagation steps) and (ii) the formation of carbon–carbon bonds, either inter- or intra-molecularly [1]. Such chain processes have been carried out by using tributyltin [2] and tributylgermanium [3] hydrides and, more recently, tris(trimethylsilyl)silane [4], and tris(alkylthio)silanes [5].

$$R\cdot + X_3MH \rightarrow RH + X_3M\cdot \qquad (1)$$

$$RZ + X_3M\cdot \underset{c}{\overset{a}{\rightleftharpoons}} [R\dot{Z}MX_3] \xrightarrow{b} R\cdot + X_3MZ \qquad (2)$$

The most important consideration in selecting different reducing agents for these processes concerns the relative hydrogen-donor abilities of the hydrides [6*]. It is well known that alkanethiols are rather good H-atom donors towards alkyl radicals [7] and that silyl radicals are amongst the most reactive species known for halogen abstraction [8,9] and for addition to double and triple bonds [10]. This suggests that any class of compounds with an appropriate molecular arrangement which allows the transformation of a thiyl to a silyl radical via a fast intramolecular rearrangement will potentially be a good radical-based reducing agent [11*]. In continuation of our exploration of the use of organosilanes as radical-based reducing agents, aimed at obtaining compounds with increased selectivity and/or reactivity, we decided to examine the compounds $(Me_3Si)_3Si(CH_2)_nSH$ (**1**). We report here our preliminary work on the compound with $n = 0$, i.e. tris(trimethylsilyl)silanethiol, **2**. We expected that this new reagent might be an important tool for organic chemists.

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Reduction of some cyclohexyl derivatives by silane **3** and thiol **2** [a]

Substrate, RZ	$(Me_3Si)_2Si(H)SSiMe_3$			$(Me_3Si)_2Si(H)SSiMe_3$			$(Me_3Si)_3SiSH$		
	t (min)	conv. (%)	yield (%)	*t* (min)	conv. (%)	yield (%)	*t* (min)	conv. (%)	yield (%)
cyclo-$C_6H_{11}Br$	30	100	97	5	74	98	5	100	94
cyclo-$C_6H_{11}I$	30	100	99	5	78	98	5	100	99
cyclo-$C_6H_{11}NC$	30	100	98	5	89	97	5	100	85
cyclo-$C_6H_{11}OC(S)SMe$	30	100	99	5	47	99	5	48	88
cyclo-$C_6H_{11}SePh$	30	72	99	5	13	99	5	4	99

[a] General procedure: a solution containing 0.30 *M* organic substrate, the appropriate reducing agent (0.36 *M*) and a catalytic amount of AIBN (5–7%) in toluene was heated at 85 °C and then analysed by GC. Conversions and yields were quantified by GC using decane as an internal standard. Conversions are based on disappearance of the starting material. Yields are based on the formation of cyclohexane and on the amount of substrate converted.

Tris(trimethylsilyl)silanethiol was prepared in a one-pot reaction from the corresponding commercially available silane in 95% overall yield [12*]:

$$(Me_3Si)_3SiH \xrightarrow{CCl_4} (Me_3Si)_3SiCl \xrightarrow{NH_3} (Me_3Si)_3SiNH_2 \xrightarrow{H_2S} \underset{(\mathbf{2})}{(Me_3Si)_3SiSH} \quad (3)$$

When heated at 80 °C in toluene containing AIBN (azobisisobutyronitrile) compound **2** rearranges to an isomeric form (74% yield) in about 15 minutes (eq. 4). The identity of the rearranged product **3** [12*] and the observation that the reaction was retarded by duroquinone (an excellent spin-trap for tris(trimethylsilyl)silyl radicals) [13] are consistent with a chain reaction in which the key step is the 1,2-shift shown in eq. 5 [14 *].

$$\underset{(\mathbf{2})}{(Me_3Si)_3SiSH} \xrightarrow[\text{toluene}]{\text{AIBN}/80\,^\circ\text{C}} \underset{(\mathbf{3})}{(Me_3Si)_2Si(H)SSiMe_3} \quad (4)$$

$$\underset{(\mathbf{4})}{(Me_3Si)_3SiS\cdot} \xrightarrow{\text{1,2-shift}} \underset{(\mathbf{5})}{(Me_3Si)_2\dot{S}iSSiMe_3} \quad (5)$$

The rearranged product **3** was expected to be a good hydrogen-atom donor in the light of our recent observations on the behaviour of on $(Me_3Si)_3SiH$ [4] and $(RS)_3SiH$ [5] as reducing agents, and this turned out to be the case. The reduction yields are shown in column 2 of Table 1 and refer to a reaction time of 30 min. The reductions were efficient for a variety of alkyl derivatives. Evidence for a free radical chain mechanism (eq. 1 and 2) was provided by the observations that the reactions were catalysed by light and by thermal sources of free radicals such as AIBN and dibenzoyl peroxide. Furthermore the reactions were retarded by 2,6-tert-butyl-4-methylphenol and duroquinone, which are inhibitors for steps 1 and 2, respectively.

Similarly, good to excellent yields of reduction products from a variety of organic substrates were also obtained when tris(trimethylsilyl)silanethiol was used under the same experimental conditions and so it might be argued that thiol **2** rearranges to silane **3** (eq. 4) prior to the reduction process. However, when we ran the two sets of reactions for 5 min (see the data in columns 3 and 4, respectively of Table 1), it

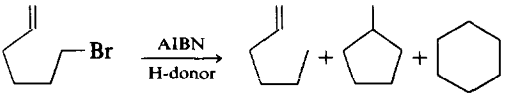
Table 2

Data referring to the reaction 6 [a]

H-donor	*t* (min)	conv. (%)	yield (%)	ratio **6**:**7**:**8**
$(Me_3Si)_2Si(H)SSiMe_3$	5	10	100	2:34:1
$(Me_3Si)_2Si(H)SSiMe_3$	30	77	96	3:36:1
$(Me_3Si)_3SiSH$	5	51	99	62:35:1
Bu_3SnH	5	31	100	32:33:1
$(Me_3Si)_3SiH$	5	35	99	2.5:31:1

[a] General procedure: a solution containing 0.1 *M* of 5-hexenyl bromide, the appropriate reducing agent (0.12 *M*) and a catalytic amount of AIBN when necessary in toluene was heated at 85 °C and then analysed by GC. Conversions and yields were quantified by GC using decane as an internal standard and refer to average values of multiple runs. Conversions are based on disappearance of the starting material. Yields are based on total hydrocarbon formation and on the amount of substrate converted.

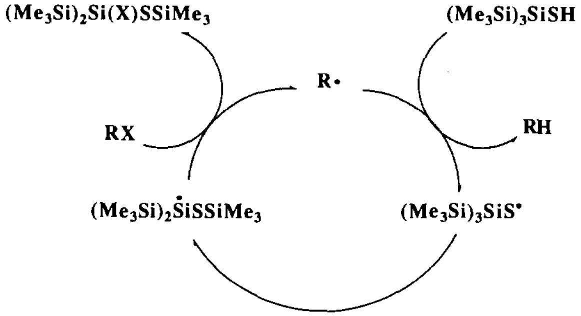
became evident that the behaviours of the two reducing agents are different, at least for reduction of cyclohexyl bromide and iodide. In view of the relevance of mechanistic knowledge for planning synthetic applications, we carried out the reduction of 5-hexenyl bromide; in particular, the ratios of cyclized/uncyclized products (cf. eq. 6) were determined under various conditions using both **2** and **3**, as well as Bu_3SnH and $(Me_3Si)_3SiH$ for comparison. The data in Table 2 indicate that thiol **2** is an excellent hydrogen-atom donor towards alkyl radicals and so we suggest for the reduction of alkyl bromides and iodides the mechanism outlined in Scheme 1.



(6) **(7)** **(8)**

(6)

We have recently shown [4] that in the reduction of alkyl isocyanides, xanthates, selenides with $(Me_3Si)_3SiH$, the key steps of the chain reactions are the fragmentations of intermediate radicals derived from the fast addition of $(Me_3Si)_3Si\cdot$ radicals to the specific substrates (cf. eq. 2, where $R\dot{Z}MX_3$ represent a radical adduct). Whereas for isocyanides the reverse of the addition (eq. 2c) is unimportant, for



Scheme 1

xanthates and selenides such a process is efficient [4]. If we make the reasonable assumption that the behaviour of $(Me_3Si)_3Si\cdot$ and $(Me_3Si)_2\dot{S}iSSiMe_3$ radicals towards organic functions are similar, then on the basis of the data of Table 1 we can suggest that the reduction of cyclohexyl isocyanide proceeds via the mechanism reported in Scheme 1, whereas for cyclohexyl xanthate or selenide such a mechanism is either unimportant or does not occur at all.

In conclusion, tris(trimethylsilyl)silanethiol functions as a free-radical reducing agent for some organic substrates, and its main feature is that it is an excellent hydrogen donor. Further work is in progress on this material and on $(Me_3Si)_3Si(CH_2)_nSH$ compounds with $n = 1, 2, 3, 4$ as radical-based reducing agents.

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