

Tris(alkylthio)silanes as New Reducing Agents via Radicals

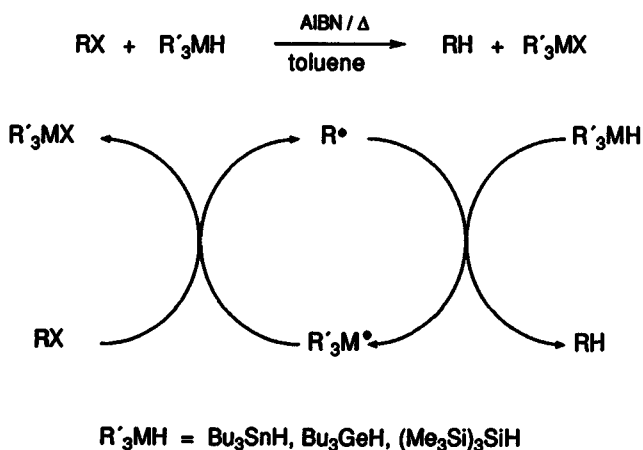
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Received 27 December 1989

Abstract: Tris(methylthio)silane and tris(isopropylthio)silane effectively reduce a variety of organic substrates in the presence of a radical initiator. They appear to be good alternatives to trialkylgermanium hydrides in radical chain reactions.

It has been recently shown that tris(trimethylsilyl)silane¹⁻⁴ is an attractive alternative to tributyltin hydride⁵ in some radical chain reductions (see Scheme 1). We have continued to explore the use of silicon hydrides as radical-based reducing agents in order to obtain compounds with increased selectivity and/or reactivity.



Scheme 1

Trialkylgermanium hydrides are less reactive hydrogen donors than their tin analogs, while the corresponding germyl radicals are at least as reactive as stannyl radicals in reactions with organic substrates.⁶ However, due mainly to the high cost of germanium hydrides, tin hydrides have been used in low concentrations to achieve similar results.⁷ Developing our original idea^{8,9} on the influence of adjacent heteroatoms on the strength of silicon-hydrogen bonds, we considered that tris(alkylthio)silanes might be good hydrogen donors and that these compounds would be capable of sustaining radical chain reactions. Our choice of alkylthio as the substituent on silicon was guided not only by the low electronegativity of sulfur but also by the possibility that 3p-3p overlap could be effective in the corresponding silyl radicals.¹⁰ Our expectation turned out to be correct, and we now report our preliminary work on the use of $(\text{MeS})_3\text{SiH}$ and $(i\text{-PrS})_3\text{SiH}$ which are new and potentially valuable reducing agents operating via a free radical chain process.

Tris(methylthio)silane and tris(2-propylthio)silane were prepared in yields of 40% and 60% respectively, using trichlorosilane, pyridine and alkanethiols (eq. 1).^{11,12} Good to

excellent yields of reduction products from a variety of organic substrates were obtained using tris(methylthio)silane and tris(2-propylthio)silane. Some representative data are given in Table 1. In general, the reductions were very efficient for alkyl bromides, iodides, isocyanides, selenides and xanthates, but were somewhat less efficient for alkyl chlorides and sulphides.¹³

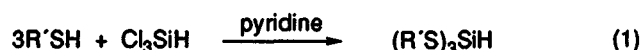
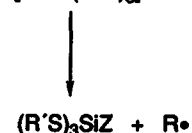
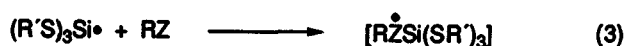


Table 1. Reduction of some organic compounds by tris(alkylthio)silane^a

Compound	$(\text{MeS})_3\text{SiH}$		$(i\text{-PrS})_3\text{SiH}$	
	conv.% ^b	yield% ^c	conv.% ^b	yield% ^c
$\text{CH}_3(\text{CH}_2)_{15}\text{Br}$	100	94	100	94
$\text{CH}_3(\text{CH}_2)_{15}\text{I}$	100	97	100	98
$c\text{-C}_6\text{H}_{11}\text{NC}$	92	96	85	79
$c\text{-C}_6\text{H}_{11}\text{OC(S)SMe}$	78	97	80	98
$c\text{-C}_6\text{H}_{11}\text{SePh}$	95	98	96	99

^a For general procedure see reference 16. ^bConversions by GC analysis based on consumption of starting material. ^cYields by GC analysis based on formation of RH.

Evidence for a free radical chain mechanism (eq. 2 and 3) was provided by the observations that the reactions were catalyzed by light and by thermal sources of free radicals such as azobisisobutyronitrile and dibenzoyl peroxide. Furthermore the reactions were retarded by 2,6-*tert*-butyl-4-methylphenol and duroquinone, which are inhibitors of steps 2 and 3, respectively. Structure $[\text{RZSi}(\text{SR}')_3]$ represents a reactive intermediate or a transition state.¹⁴



Based on a proposed correlation⁸ between bond dissociation energies of trisubstituted silanes, i.e. $BDE(X_3Si-H)$, and the sum of substituent group electronegativities, i.e. $\sum\chi^x$, a bond strength of 82-83 kcal mol⁻¹ is predicted for $(MeS)_3Si-H$. This value is similar to the BDE of trialkylgermanium hydrides.¹⁵ Thus tris(alkylthio)silanes are effective reducing agents of organic substrates and offer a cheaper alternative to trialkylgermanium hydrides.⁶

Acknowledgement. We thank Prof. B. Giese and Dr. D. Griller for helpful discussions. We also thank the Italian Progetto Finalizzato "Chimica Fine II" (CNR - Rome) for financial support.

References and Notes

- (1) Chatgililoglu, C.; Lesage, M.; Griller, D. *J. Org. Chem.* **1988**, *53*, 3641.
- (2) Giese, B.; Kopping, B.; Chatgililoglu, C. *Tetrahedron Lett.* **1989**, *30*, 681.
- (3) Chatgililoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1989**, *54*, 2492.
- (4) Lesage, M.; Chatgililoglu, C.; Griller, D. *Tetrahedron Lett.* **1989**, *30*, 2733.
- (5) For recent reviews on the tributyltin hydride as a reducing agent, see: Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 533; Newmann, W.P. *Synthesis* **1987**, 665; Curran D.P. *Synthesis*, **1988**, 417 and 489.
- (6) Luszyk, J.; Maillard, B.; Deycard, S.; Lindsay, D.A.; Ingold, K.U. *J. Org. Chem.* **1987**, *52*, 3509 and references therein.
- (7) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, Pergamon Press: Oxford, 1986.
- (8) Chatgililoglu, C. in *Free Radicals in Synthesis and Biology*, Minisci, F., Ed.; Kluwer: Dordrecht, 1989; pp 115-123.
- (9) Kanabus-Kaminska, J.M.; Hawari, J.A.; Griller, D.; Chatgililoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267.
- (10) In this respect, it is worth mentioning that tris(alkylthio)silyl cations were also recently reported to be the first silycenium ions in solution. (see: Lambert, J.B.; Schulz, Jr., W.J.; McConnell, J.A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201).
- (11) Wolinski, L.; Tieckelmann, H.; Post, H.W. *J. Org. Chem.* **1951**, *16*, 395.
- (12) These compounds are very unpleasant and they can cause severe headaches. They should be handled carefully and used with adequate ventilation.
- (13) For alkyl chlorides and sulphides, although the yields are relatively high, the conversions are rather low. This is probably due to the chain length of the reaction being too short.
- (14) Evidence have been obtained that in the reaction of tris(trimethylsilyl)silane with halides $[R\dot{Z}Si(SR')_3]$ represents a transition state³ whereas with isocyanides and xanthates $[R\dot{Z}Si(SR')_3]$ is a reactive intermediate (Chatgililoglu, C. unpublished data).
- (15) Jackson, R.A. *J. Organomet. Chem.* **1979**, *166*, 17.
- (16) General procedure: a solution, containing the compound to be reduced, tris(alkylthio)silane (1.2 eq.) and a catalytic amount of AIBN in toluene was heated at 75-90°C for 0.5-2h and then analyzed by GC. Yields and conversions were quantified by GC using tetradecane as an internal standard.