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SULFUR

in Organic and Inorganic Chemistry

Edited by

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Volume 4

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SULFUR

**in Organic and
Inorganic Chemistry**

Preface

Today, approximately 10 years after the first three volumes were published, it is gratifying to note that the Editor's concept realized in Sulfur in Organic and Inorganic Chemistry with the generous help of many prominent and creative authors has achieved its aims as evidenced by the many references to its reviews in a steady stream of contemporary research papers.

It is this very activity in the field of sulfur research which clearly necessitates a new volume of Sulfur in Organic and Inorganic Chemistry. It covers the results of another decennium of sulfur research employing the same style and organization as Volume 1. For reasons beyond the Editor's control, unfortunately, only seven of the nine chapters of Volume 1 could be updated in time for inclusion in Volume 4.

The Editor takes pride in acknowledging the continued support and co-operation of four stalwarts among the authors of Volume 1 who were willing to contribute a second crop of expert reviews and at the same time welcomes the three new distinguished authors who agreed to join the panel of contributors to Volume 4.

Alexander Senning

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The Sulfur-Sulfur Bond, John L. Kice

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1

The Sulfur-Silicon Bond

Alois Haas / Reiner Hitzte

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I. Introduction	1
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I. INTRODUCTION

This chapter covers the literature up to 1979 and gives a systematic view of recent developments and progress in the chemistry of the silicon-sulfur bond. It is a continuation of and a supplement to our chapter in Volume 1 of this series [1]. A complete review has been published in [2]. No progress was achieved in Si-S chemistry with sulfur in the oxidation states +4 and +6. Silyl sulfoxides and sulfones are still unknown. However, progress was made in proving the existence of a Si-S double bond in some species which appear as reactive intermediates.

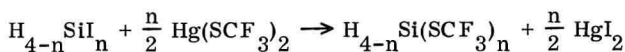
II. SILICON-SULFUR COMPOUNDS WITH SULFUR IN THE OXIDATION STATE -2

This class of compounds can be divided into the following two groups:

1. noncyclic moieties
2. cyclic moieties

In the first group of compounds new CF_3S -substituted silanes were synthesized and characterized, so that in the series $\text{H}_{4-n}\text{Si}(\text{SCF}_3)_n$ all four members are known. The substance with $n = 1$ is already known since 1960, when Downs and Ebsworth treated SiH_3I with $\text{Hg}(\text{SCF}_3)_2$ and obtained H_3SiSCF_3 [3]. This replacement of iodine in iodosilanes was also used to

prepare the other members. For $n = 2$ and 3 decalin was used as a solvent, and for $n = 4$ carbon disulfide was used.



$$n = 1 [3], 2, 3, 4 [4]$$

These mercaptosilanes are sensitive to moisture and decompose slowly at room temperature when kept in a sealed tube in a pure state. Their stability increases with increasing n . In the presence of catalysts such as Al_2S_3 and mercury halides they decompose according to $\text{H}_{4-n}\text{Si}(\text{SCF}_3)_n \rightarrow \text{H}_{4-n}\text{SiF}_n + n \text{SCF}_2$.

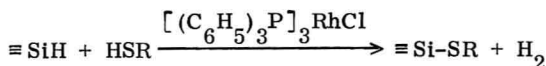
The reaction mechanism for a β -elimination of β -chloroalkylsilanes in the presence of Al_2Cl_6 given by Sommer, Bailey, and Whitmore [5] can be used to explain this decomposition process. ^{29}Si , ^{19}F , and ^1H chemical shifts and coupling constants for $\text{H}_{4-n}\text{Si}(\text{SCF}_3)_n$ are given in the following table.

$(\text{CF}_3\text{S})_n\text{SiH}_{4-n}$	^{29}Si δ	^{19}F δ	^1H δ	$J_{\text{Si-H}}$	$J_{\text{F-H}}$	$J_{\text{Si-F}}$
$n = 1$	-53.1	31.2	4.42	234 Hz	1.75 Hz	6.14 Hz
$n = 2$	-22.8	31	5.44	270 Hz	2.02 Hz	4.15 Hz
$n = 3$	0.63	27.8	6.36	331 Hz	1.65 Hz	7.10 Hz
$n = 4$	11.3	27	--	--	--	5.15 Hz

Internal references: $\text{Si}(\text{CH}_3)_4$ (^1H , ^{29}Si) and CFCI_3 (^{19}F).

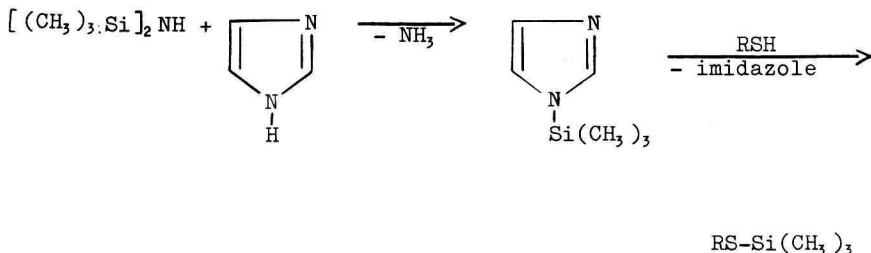
The ^{29}Si NMR chemical shifts show a steady low-field shift with increasing number of CF_3S groups in the molecule [4]. This continuous decrease of charge density at the silicon atom indicates, if anything, only a small $p\pi$ - $d\pi$ back-bonding effect. A similar trend was observed in the $(\text{CH}_3)_n\text{Si}(\text{SCH}_3)_{4-n}$ series [6].

Tris-(triphenylphosphine)-chlororhodium catalyzes the dehydrogenative condensation of hydrosilanes and thiols



The rate of reaction is dependent upon the nature of the thiol and the hydrosilane. Dihydrosilanes are much more reactive than monohydrosilanes, and yield monohydrosilyl sulfides. The reactivity order is $(\text{C}_2\text{H}_5)_2\text{SiH}_2 < \text{C}_6\text{H}_5(\text{CH}_3)\text{SiH}_2 < (\text{C}_6\text{H}_5)_2\text{SiH}_2$. Thiophenol reacts similarly to benzyl mercaptan, and distinctly faster than alkanethiols. A phenyl substituent on silicon increases the reactivity; for example, $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiH}$ reacts eight

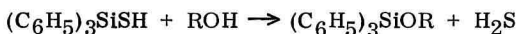
times faster than $(\text{C}_2\text{H}_5)_3\text{SiH}$ with $\text{C}_6\text{H}_5\text{SH}$ in C_6H_6 at 20°C [7]. Another catalyzed reaction for the preparation of trimethylsilyl sulfides is the condensation of $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ with thiols in the presence of imidazoles. The silylation occurs as follows:



$\text{R} = \text{CH}_3(\text{CH}_2)_9-$, $\text{HS-CH}_2\text{CH}_2-$ (double silylation), $(\text{C}_6\text{H}_5)_2\text{CH-}$, C_6H_5- , $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2-$, $\text{CH}_3(\text{CH}_2)_2\text{C}(\text{CH}_3)_2-$, $(\text{CH}_2)_4\text{C}(\text{CH}_3)-$, $(\text{CH}_2)_5\text{CH-}$ [8].

Investigations of the hydrolysis of silanethiols such as R_3SiSH and $(\text{RO})_3\text{SiSH}$ show that the charge density at the Si atom has a strong effect on the stability of the Si-S bond towards solvolysis. With increasing electron density at the Si atom, the stability of the Si-S bond toward hydrolysis increases [9]. Since hydrolysis of silanethiols occurs according to an $\text{S}_\text{N}2$ mechanism with inversion, as proven with $\text{CH}_3(\text{C}_6\text{H}_5)\alpha\text{-naphthyl-SiSR}$ ($\text{R} = \text{H}, \text{CH}_3, \dots$) by Sommer and McLick [10], steric effects influence the reaction rate as well. Bulky substituents make the transition of a tetra- to a pentacoordinated Si atom more difficult. Therefore $(o\text{-Tol})_3\text{SiSH}$ is stable towards a dioxane/ H_2O mixture for 100 hr at $25\text{--}55^\circ\text{C}$ [9].

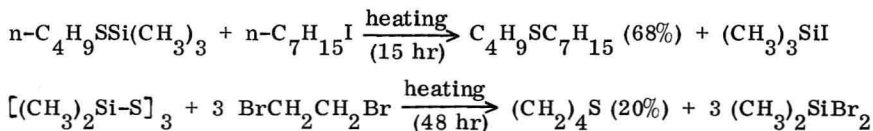
In alcoholysis reactions, additional effects such as the structure of the alcohol influence the reaction rate of the solvolysis. With $(\text{C}_6\text{H}_5)_3\text{SiSH}$, alcohols react according to



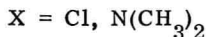
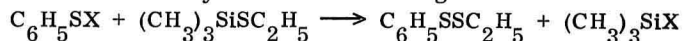
With CH_3OH the reaction is faster than with $\text{C}_2\text{H}_5\text{OH}$ or $n\text{-C}_3\text{H}_7\text{OH}$. Normal alcohols react faster than branched and secondary alcohols. No reaction was observed with $(\text{CH}_3)_3\text{COH}$. Solvolysis with $\text{C}_6\text{H}_5\text{OH}$ is slower than with cyclohexanol, and *o*-cresol reacts faster than phenol. In summary, it can be said that alcohols with bulky groups do not react at all or react much more slowly than others [11]. Triphenyl- and trimethylsilanethiol are stronger Lewis and Brönsted acids than their carbon analogs. The relative Brönsted acidity—measured by potentiometric titration and characterized by the half-neutralization potential—is as follows: $(\text{C}_6\text{H}_5)_3\text{SiSH} > \text{C}_6\text{H}_5\text{SH} > (\text{C}_6\text{H}_5)_3\text{CSH} > \text{C}_6\text{H}_5\text{OH} > (\text{C}_6\text{H}_5)_3\text{SiOH} > (\text{CH}_3)_3\text{SiSH}, (\text{CH}_3)_3\text{CSH}$ [12]. When the Brönsted acidity of trialkoxysilanethiols was investigated in the

same way the series could be expanded as follows: $[(CH_3)_2CHO]_3SiSH > (cycl. -C_6H_{11}O)_3SiSH > (C_6H_5)_3SiSH > C_6H_5C(O)OH > (s-BuO)_3SiSH > (s-n-AmO)_3SiSH > (s-i-AmO)_3SiSH > C_6H_5SH > (t-BuO)_3SiSH$ [13]. These results show that alkoxy groups decrease the electrophilic character of the Si atom and stabilize the Si-S bond.

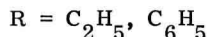
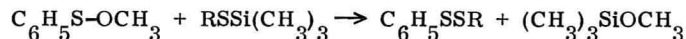
The reactivity of the Si-S bond can be employed in preparative chemistry. Alkyl halides and α, ω -dihaloalkanes (preferentially bromides and iodides) react with *n*-alkylthiotrimethylsilanes, hexamethyldisilthiane, and hexamethylcyclotrisilthiane to give linear and cyclic organic sulfides, respectively. For example [14]



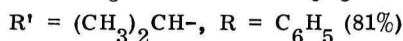
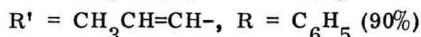
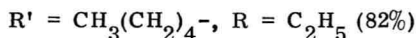
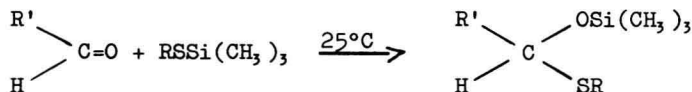
Trimethyl-(alkylthio)-silanes react with *N,N*-dimethylbenzenesulfenamide or benzenesulfonyl chloride according to



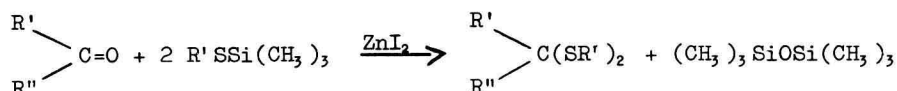
Unsymmetrical disubstituted disulfides can also be prepared in good yield via the reaction



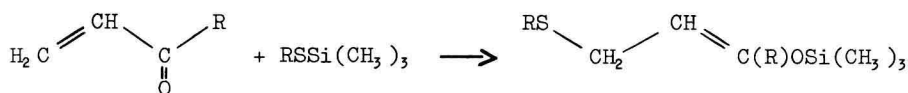
The formation of low boiling $(CH_3)_3SiCl$ and $(CH_3)_3SiOCH_3$, respectively assists separation in these strongly thermodynamically favored reactions [15]. A selective carbonyl protection under mild conditions can be achieved using alkyl- or arylthiosilanes $[RSSi(CH_3)_3]$. Aldehydes react in the presence of catalytic amounts of a nucleophile (CN^-, F^-) with $RSSi(CH_3)_3$ according to



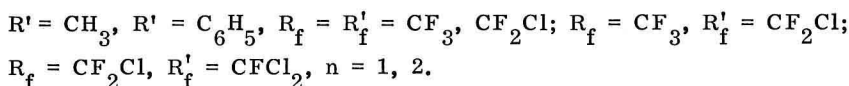
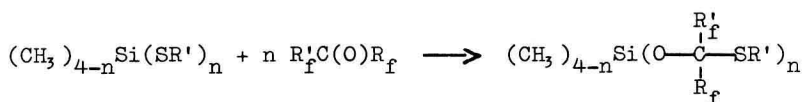
In the absence of catalysts, elevated temperatures (120–130°C; 10 to 20 hr) are needed. In the presence of Lewis acids such as ZnI_2 , ketones add $\text{RSSi}(\text{CH}_3)_3$ to form thioketals and $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$



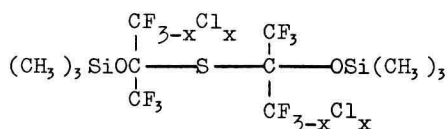
α, β -Unsaturated aldehydes and ketones react exothermically with $\text{RSSi}(\text{CH}_3)_3$ in the presence of CN^- , F^- , or RS^- at 25°C. In every case examined, 1,4-addition was observed [16]:



Perfluorochloroacetones cleave the Si-S bond in $\text{R}_{4-n}\text{Si}(\text{SR}')_n$ and $\text{R}_3\text{SiSSiR}_3'$ to form the corresponding alkoxy silanes



A double insertion takes place with $(\text{CH}_3)_3\text{SiSSi}(\text{CH}_3)_3$ and $\text{CF}_3\text{C}(\text{O})\text{CF}_{3-x}\text{Cl}_x$:



$$x = 0, 1$$

These reactions take place under mild conditions (70°C) and produce good yields (90%). Neither acetone nor $\text{CF}_3\text{C}(\text{S})\text{CH}_3$ reacted with alkylthio-silanes despite rigorous conditions and long reaction times. Hexachloroacetone produces no isolatable insertion product, but much $(\text{CH}_3)_3\text{SiCl}$ [17]. Similar insertion reactions occur with oxygen heterocycles, according to

