CHEMISTRY LETTERS, pp. 329-332, 1979. Published by the Chemical Society of Japan

FACILE REDUCTION OF SULFOXIDES AND SULFIMIDES WITH THIOL/TRIMETHYLSILYL CHLORIDE SYSTEM

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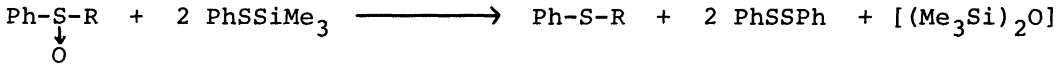
Sulfoxides were found to be deoxygenated slowly with thiosilane ($PhSSiMe_3$), while deoxygenation of sulfoxides with the thiosilane proceeded smoothly in the presence of a catalytic amount of tetra-butylammonium bromide. For a preparative purpose, a mixed system of thiol and trimethylsilyl chloride can be used successfully for both deoxygenation of sulfoxides and deimination of sulfimides.

Recently, it was reported that treatment of carbonyl compounds with thiosilane ($RSSiMe_3$) gave O-trimethylsilyl hemithioacetals(ketals) via an initial O-silylation and subsequent nucleophilic addition of the thiolate.$^{1)}$ Thus the thiosilane is considered to be a composite of a good oxygenophilic silyl group and a strong nucleophilic thiolate group, and should be able to reduce sulfoxides, since reduction of sulfoxides with sulfhydryl compounds is known to proceed through an initial protonation of sulfinyl oxygen and subsequent nucleophilic attack of thiolate on sulfonium sulfur atom.$^{2)}$ We now wish to report here that sulfoxides were indeed found to be reduced with the thiosilane.

When alkyl phenyl sulfoxide was treated with about two equivalent amounts of phenylthiotrimethylsilane at room temperature under argon atmosphere, the deoxygenation of sulfoxide was found to take place slowly (eq. 1), while upon addition



$$\text{Ph-}\underset{\downarrow\atop \text{O}}{\text{S}}\text{-R} + 2\ PhSSiMe_3 \longrightarrow \text{Ph-S-R} + 2\ PhSSPh + [(Me_3Si)_2O] \qquad (1)$$

of a catalytic amount of $Bu_4N^+Br^-$ (1/10 equivalent amount of sulfoxide) to this system, the deoxygenation with the thiosilane took place smoothly, indicating that bromide ion acts as a catalyst for heterolysis of the S-Si bond of the thiosilane, resulting in the facile O-silylation of the sulfinyl oxygen atom. These results are listed in Table 1.

Table 1 Reduction of Sulfoxide with $PhSSiMe_3$ a)

R-S(O)-R'		Additive	Time	Products (isolated yield, %) b)		
R	R'		(h)	R-S-R'	PhSSPh	R-S(O)-R' (recovered)
$PhCH_2$	$PhCH_2$	-	31c)	30	32	58
$PhCH_2$	$PhCH_2$	$Bu_4N^+Br^-$	31c)	78	70	15
Ph	Et	-	50d)	17	15	67
Ph	Et	-	120d)	42	56	44
Ph	Et	$Bu_4N^+Br^-$	48d)	69	66	8

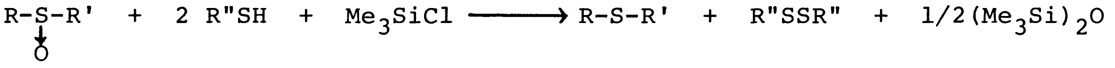
a) sulfoxide was treated with 2.3 equivalent amounts of the thiosilane at room temperature under argon atmosphere.

b) work-up method is following: reaction mixture was separated through column chromatography affording the recovered starting sulfoxide and the mixture of the sulfide and diphenyl disulfide, and the molar ratio of the mixture was determined by NMR measurements.

c) dry ether-chloroform (1/1 v/v) was used as solvent.

d) dry ether was used as solvent.

In order to facilitate the O-silylation of sulfinyl oxygen, we applied a trimethylsilyl chloride/thiol system, and found that deoxygenation of sulfoxide took place quite smoothly in high yields (eq. 2).

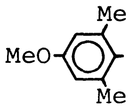
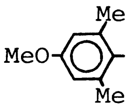


$$R\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}R' + 2\,R''SH + Me_3SiCl \longrightarrow R\text{-}S\text{-}R' + R''SSR'' + 1/2(Me_3Si)_2O \qquad (2)$$

After treatment of sulfoxides (3-4 mmole) with two equivalent amounts of benzenethiol (or alkanethiol) in 5 ml of dry ether at room temperature under argon atmosphere until the starting sulfoxide disappeared upon monitoring with TLC test, the reaction mixture was hydrolyzed with aqueous sodium bicarbonate solution,3) and then extracted with chloroform and the resulting dried chloroform solution was evaporated under reduced pressure to give the mixture of the corresponding sulfide and diphenyl disulfide, which were found to be formed nearly in quantitative yields by measurement with NMR. The sulfide and the disulfide formed were easily separated by vacuum distillation to remove one of lower volatile compound. Thus the sulfides were isolated in good yields as shown in Table 2.

Dialkyl, alkyl aryl and dibenzyl sulfoxides and ω-(p-tolylsulfinyl)acetophenone were reduced nicely within 15 min, while benzyl phenyl, diphenyl and o-substituted diaryl sulfoxides were found to be reduced substantially slowly, mainly due to lower basicity of the sulfinyl oxygen and steric bulkiness of the

Table 2 Reduction of Sulfoxide with Thiol/Me_3SiCl System

R-S(O)-R'		R"SH	Time	Products (isolated yield, %)	
R	R'		(min)	R-S-R'	R"SSR"
Ph	Et	PhSH	10	96	100
Ph	Me	PhSH	5	100	100
Bu	Bu	PhSH	5	90	100
s-Bu	Me	PhSH	5	70	100
$PhCH_2$	Me	PhSH	5	80	98
$PhCH_2$	$PhCH_2$	PhSH	5a)	(100)b)	(100)b)
$PhCH_2$	$PhCH_2$	BuSH	15a)	73	83
p-Tol	CH_2COPh	PrSH	15	90	52
$PhCH_2$	Ph	BuSH	60	82	100
$PhCH_2$	Ph	PhSH	70	(92)b)	(100)b)
Ph		PhSH	90	76	78
Ph	Ph	BuSH	(36 h)a)	98	94
		BuSH	(78 h)a)	7c)	7

a) the reaction was carried out in chloroform solution.

b) the sulfide and diphenyl disulfide cannot be separated by vacuum distillation, and the yields were estimated by NMR measurements of these mixtures.

c) the starting sulfoxide was recovered in 93% yield.

substrate.

This reducing system (thiol/Me_3SiCl) can also be applied for the reduction of sulfimides,4) and the corresponding sulfide, disulfide and p-tosylamide were obtained in good yields as shown in Table 3. (eq. 3)

$$\mathrm{R}-\underset{\substack{\downarrow\\ \mathrm{NTs}}}{\mathrm{S}}-\mathrm{R'} + 2\ \mathrm{R''SH} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{R{-}S{-}R'} + \mathrm{R''SSR''} + \mathrm{TsNH_2} \tag{3}$$

Although deoxygenation of sulfoxide after activation of O-silylation with Me_3SiI(or Me_3SiBr)5)and $(Me_3Si)_2S$6) were recently reported, the deoxygenation is accompanied with substantial side reactions (i.e., halogenation or degradation) especially with sulfoxides each having an activated methylene group, such as dibenzyl sulfoxide and ω-methylsulfinylacetophenone. Thus, we believe our system to be more convenient for preparative purposes than with other reagents which are not commonly available.

Table 3 Reduction of Sulfimides with Thiol/Me_3SiCl System a)

$R\text{-}\underset{\underset{NTs}{\downarrow}}{S}\text{-}R'$		R"SH	Time	Products (isolated yield, %) b)		
R	R'		(hr)	R-S-R'	R"SSR"	$TsNH_2$
Bu	Bu	PhSH	6	91	90	100
Ph	Me	PhSH	1.5	96	100	83
Ph	Me	PhSH	1.5 c)	73	70	90
$PhCH_2$	Me	PhSH	9	72	80	72
p-Tol	Et	PhSH	20	72	94	75
p-Tol	p-Tol	BuSH	60	83	93	79
$-(CH_2)_5-$		PhSH	8	(82) d)	81	80

a) reaction was carried out in chloroform solution at room temperature under argon atmosphere.

b) work-up method is following: tosylamide precipitated was filtered off and the filtrate was analyzed according to a similar manner in the case of sulfoxide.

c) this experiment was carried out in the presence of an equimolar amount of Me_3SiCl.

d) yield was determined by glc analysis.

References and Notes

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3. Excess trimethylsilyl chloride and $Me_3SiOSiMe_3$ formed were hydrolyzed for removing from organic layer. $Me_3SiOSiMe_3$ was found to be formed in 47% yield determined by glc analysis of the reaction mixture of dimethyl sulfoxide, PhSH (2 eq.) and Me_3SiCl (1.1 eq.).
4. Sulfimide was found to be reduced with benzenethiol alone, though substantially slowly: PhS(NTs)Me was reduced in 78% yield at room temperature for 24 h., while $(CH_2)_5S\rightarrow NTs$ was reduced partially during a long reaction time (51%, 3 days).
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(Received February 2, 1979)