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FACILE REDUCTION OF SULFINIC ACID TO DISULFIDE WITH THIOL AND CHLOROTRIMETHYLSILANE

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Sulfinic acids were found to be readily reduced to the corresponding disulfide quantitatively at room temperature upon treatment with a mixture of thiols and chlorotrimethylsilane.

Despite the numerous **studies on** the deoxygenative reduction of sulfoxides in recent years, there has been no systematic investigation on reduction of sulfinic and sulfonic acids. As one of our preliminary studies on the reductions of sulfinyl and sulfonyl compounds, we have found a facile and clean reaction of sulfinic acids with thiols in the presence of chlorotrimethylsilane giving disulfides quantitatively(eq.1). This communication deals with this reaction.

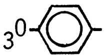
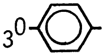
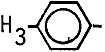
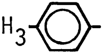
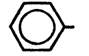
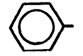
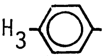
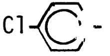
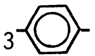
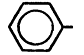
$$RSO_2H + 3\ R'SH + 4\ (CH_3)_3SiCl \longrightarrow RSSR' + R'SSR' + 2\ [(CH_3)_3Si]_2O + 4\ HCl \text{ - - - - - } (1)$$

Sulfinic acids have been known to be reduced either by electrolysis$^{1)}$, or by treatment with $LiAlH_4$$^{2)}$ to disulfides, however, these procedures are complicated while the yields are poor. The reduction of sulfonyl chlorides with thiols to the corresponding disulfides is considered to proceed via the formation of the corresponding sulfinic acids$^{3)}$. Indeed the reaction between p-toluenesulfinic acid and butanethiol has been known to afford a mixture of butyl p-tolyl disulfide and dibutyl disulfide, however, substantial amounts of S-butyl p-toluenethiosulfonate and S-p-tolyl p-toluenethiosulfonate are also formed(eq.2)$^{4)}$.

$$p\text{-}TolSO_2H + n\text{-}BuSH \longrightarrow p\text{-}TolSSBu\text{-}n + n\text{-}BuSSBu\text{-}n + p\text{-}TolSO_2STol\text{-}p + p\text{-}TolSO_2SBu\text{-}n \text{ - - - } (2)$$

In order to examine the generality of this reaction, several sulfinic acids and thiols were allowed to react under the conditions in which disproportionation of these sulfinic acids is negligible$^{5)}$. Some typical examples are listed in Table 1. With large excess of thiols, the

Table 1. Reaction of Sulfinic Acid with Thiol in CH_2Cl_2 under Reflux Condition[a)]

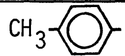
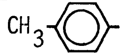
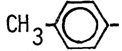
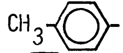
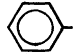
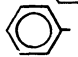
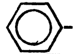
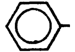
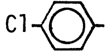
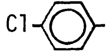
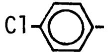
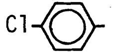
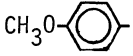
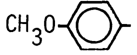
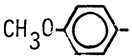
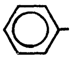
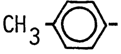
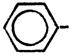
R-SO_2H	R'-SH	$\frac{[R'SH]}{[RSO_2H]}$	Time (h)	RSSR' (%)	R'SSR' (%)	RSO_2SR (%)	RSO_2SR' (%)	recovered RSO_2H (%)
CH_3O-	CH_3O-	5	19	70	-	-	0	30
CH_3-	CH_3-	5	19	73	-	-	0	4.3
		5	19	70	-	-	0	0
n-C_4H_9-	n-C_4H_9-	5	20	37	-	-	15	6.4
n-C_5H_{11}-	n-C_5H_{11}-	5	20	17	-	-	15.3	24
CH_3-	n-C_4H_9-	5	19	74	56.2	trace	9	b)
Cl-	CH_3-	5	19	80	88	0	7.7	b)
n-C_4H_9-		5	20	24	25	trace	b)	20

a) Yields were calculated based on RSO_2H. b) Not determined.

reaction proceeded at a moderate rate upon heating and gave predominantly disulfides, however, the reaction of either arenesulfinic acids bearing electron-donating group or alkanesulfinic acids were found to proceed slowly and give substantial amounts of thiosulfonic S-ester.

Meanwhile we found recently that sulfoxides can be reduced to the corresponding sulfides by treating with thiols in the presence of chlorotrimetnylsilane. Apparently silylation of sulfinyl oxygen activated the sulfur atom to be susceptible to the nucleophilic attack of thiols[6)]. This thiol/chlorotrimethylsilane system has been found again to be quite effective in the reduction of sulfinic acids, the reaction shown by eq.1 being completed within an hour at room temperature. This reduction procedure can be applied to all kinds of sulfinic acids including alkanesulfinic acids, sterically hindered ones and those bearing electron-donating substituents, most of which are difficult to be reduced by the normal treatment to the corresponding disulfides quantitatively. Depending on the sequence of mixing of the reactants, the reaction products were found to be somewhat changed. Namely, when chlorotrimethylsilane was added into a mixture of thiol and sulfinic acid, substantial amounts of thiosulfonic S-ester was formed as a by-product (procedure-1). However, when sulfinic acid was allowed to react with chlorotrimethylsilane for 1 h at room temperature and then thiol was added into the reaction mixture, the formation of disulfide was found to be almost quantitatively accompanying only a few or no thiosulfonic S-ester (procedure-2). In the reaction of procedure-2, the key intermediate was found to be sulfinyl chloride, since treatment of a mixture of p-toluenesulfinic acid and chlorotrimethylsilane for 30 min in $CHCl_3$ gave quantitatively p-toluenesulfinyl chloride(eq.3), which upon treatment with p-toluenethiol(eq.4) at room temperature yielded di-p-tolyl disulfide quantitatively.

Table 2. Reaction of Sulfinic Acid with Thiol/Chlorotrimethylsilane at Room Temperature in $CHCl_3$[a)]

$R\text{-}SO_2H$	$R'\text{-}SH$	$\frac{[R'SH]}{[RSO_2H]}$	Time (h)	RSSR' (%)	R'SSR' (%)	RSO_2SR (%)	RSO_2SR' (%)
		5	0.5[b)]	89	-	-	8
		5	1+0.5[c)]	99	-	-	1
		5	0.5[b)]	80	-	-	13
		5	1+0.5[c)]	95.4	-	-	4.7
		5	0.5[b)]	85	-	-	7
		5	1+0.5[c)]	100	-	-	0
		5	0.5[b)]	80.4	-	-	6
$n\text{-}C_5H_{11}\text{-}$	$n\text{-}C_5H_{11}\text{-}$	5	1[b)]	92	-	-	0
$n\text{-}C_4H_9\text{-}$	$n\text{-}C_4H_9\text{-}$	5	1[b)]	89	-	-	0
mesitylene-	mesitylene-	5	1[b)]	98	-	-	0
		5	0.5[b)]	59[d)]	88	0	6
		5	1+0.5[c)]	87	100	0	0

a) $[\text{Sulfinic Acid}]/[Me_3SiCl]=1/5$. b) Procedure-1. c) Procedure-2.

d) Disproportionation product $[(p\text{-}CH_3OC_6H_4S)_2]$ was also obtained 11% yield.

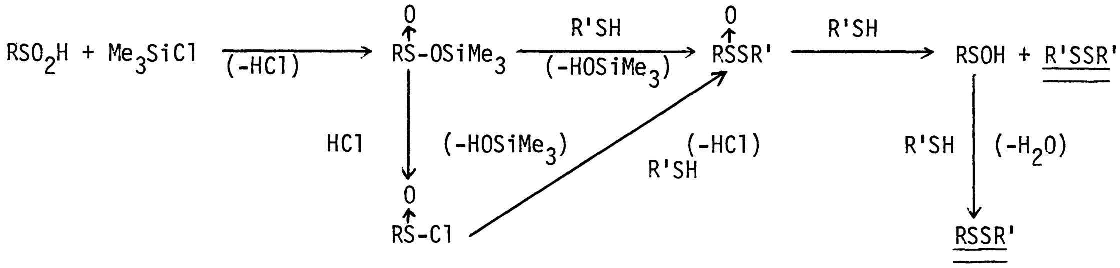
$$p\text{-}TolSO_2H + 2\ (CH_3)_3SiCl \xrightarrow[\text{in } CHCl_3]{\text{r.t. 30 min}} p\text{-}TolSOCl + [(CH_3)_3Si]_2O + HCl \text{ - - - - - - - - } (3)$$

$$p\text{-}TolSOCl + 3\ p\text{-}TolSH \xrightarrow[\text{in } CHCl_3]{\text{r.t. 15 min}} 2\ p\text{-}TolSSTol\text{-}p + H_2O + HCl \text{ - - - - - - - - - - - } (4)$$

$$p\text{-}TolSO_2Si(CH_3)_3 + PhSH \xrightarrow[\text{in } CHCl_3]{\text{r.t. 15 min}} \underset{6.3\%}{p\text{-}TolSSPh} + \underset{4\%}{PhSSPh} + \underset{1.9\%}{p\text{-}TolSO_2STol\text{-}p} + \underset{4\%}{p\text{-}TolSO_2SPh}$$

$$+ H_2O + [(CH_3)_3Si]_2O \text{ - - - - - - - - } (5)$$

Trimethylsilyl sulfinate is expected to be formed initially in the reaction of both procedures. In order to examine the behavior of trimethylsilyl sulfinate toward the thiol, trimethylsilyl p-toluenesulfinate was prepared by treating silver p-toluenesulfinate with chlorotrimethylsilane and then treated with benzenethiol. A mixture of the disulfides and the thiosulfonic S-ester were obtained as shown in eq.5[7)]. The results shown in eqs.3-5 suggest clearly that the thiosulfonic S-ester is formed by the reaction of benzenethiol with trimethylsilyl p-toluenesulfinate which is presumed to be formed in the reduction of sulfinic acid with thiol/chlorotrimethylsilane system. All these observations suggest the following mechanism for the reduction of sulfinic acids with a mixture of thiol/chlorotrimethylsilane. The control experiment of the reaction between the thiolsulfinate which is assumed to be one of key intermediates in the reaction of the sulfinic acid with a mixture of thiol/chlorotrimethylsilane, and the thiol gave only disulfide, but no thiosulfonic S-ester. The different products distributions between the two procedures depend on whether thiol is present or not when trimethylsilyl sulfinate is formed by the reaction of sulfinic acid with chlorotrimethylsilane. In the procedure-2, most trimethylsilyl sulfinate reacts with chloride anion to give sulfinyl chloride prior to the addition of thiol and eventually affords disulfide almost quantitatively by the reaction with thiol. On the other hand, since thiol is already present in the reaction system when trimethylsilyl sulfinate is formed in the procedure-1, substantial amounts of thiosulfonic S-ester is formed by the reaction between trimethylsilyl sulfinate and thiol.



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4) J. L. Kice and Eva H. Morkved, J. Amer. Chem. Soc., 85, 3472(1963).

5) J. L. Kice and K. W. Bowers, ibid., 84, 605(1962).

6) T. Numata, H. Togo and S. Oae, Chem. Lett., 1979, 329.

7) The yields are calculated based on starting silver p-toluenesulfinate. The low yields of the products were due to recovery of a large amount of p-toluenesulfinic acid. Trimethylsilyl p-toluenesulfinate was so sensitive to moisture that most of trimethylsilyl p-toluenesulfinate was hydrolyzed to give starting p-toluenesulfinic acid by action of moisture during the filtration of silver chloride before the treatment with benzenethiol.

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