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Facile Conversion of Thiosulfinic *S*-Ester to Sulfinic Ester

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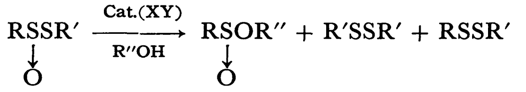
Synopsis. Thiosulfinic *S*-esters are readily converted to the corresponding sulfinic eaters in good yields by treating in alcohols with a catalytic amount of I_2, Br_2, or HCl in the presence of H_2O_2, replacing sulfenyl groups by alcohols. The mechanism of this reaction is also discussed.

Thiosulfinic *S*-esters (thiolsulfinates) have generally been considered to be unstable and to disproportionate readily.[1] Meanwhile, thiolsulfinates were shown by us to be selectively oxidized with $NaIO_4$ to the corresponding stable thiosulfonic *S*-esters (thiolsulfonates) in nearly quantitative yields. In the oxidation in aqueous alcohols, however, considerable amounts of the corresponding sulfinates were also obtained as by-products. Yields of the sulfinates were high with primary alcohols but low with tertiary alcohols.[2] We have studied on the reaction to form the alkyl sulfinates in connection with our investigation on the mechanism of the selective oxidation of the thiolsulfinates.

This paper describes facile transformation of thiolsulfinates to the corresponding stable sulfinates by replacing sulfenyl groups with alcohols, in the treatment with catalytic I_2, Br_2, or HCl in appropriate alcohols in the presence of H_2O_2. Therefore, this transformation would be quite useful for elucidation of the structure of the original thiolsulfinate and also for estimation of the amount of the unstable thiolsulfinate.

When an unsymmetrical thiolsulfinate (**1**, 1.0 mmol) was treated with a small amount of I_2, Br_2, or HCl (3—40 mg, see Table 1) in excess alcohol (5—10 ml) as a solvent at r.t., the sulfinate **2**, in which the sulfenyl group is replaced by the alcohol used, was readily (within 2 h) obtained in 61—70% yields, along with considerable amounts of disulfides (**3** and **4**) (Eq. 1). Yields of the products were determined by GLC and NMR. When acetonitrile was used as a solvent instead of alcohol, thiolsulfinate disappeared more readily than in alcohol, but afforded the disproportionation products (a mixture of disulfides and thiolsulfonates).



$$\underset{\substack{\downarrow\\ O}}{RSSR'} \xrightarrow[R''OH]{Cat.(XY)} \underset{\substack{\downarrow\\ O}}{RSOR''} + R'SSR' + RSSR' \qquad (1)$$

1 **2** **3** **4**

$$XY = I_2, Br_2, HCl$$

When an equimolar or excess amount of H_2O_2 was added into the reaction system besides the catalyst, the yield of **2** increased dramtically (entries 10—12), and the formation of unsymmetrical disulfide (**4**) was markedly reduced. Thus, the thiolsulfinate **1** was readily transformed to the corresponding stable sulfinate **2** in high yield (Eq. 2).

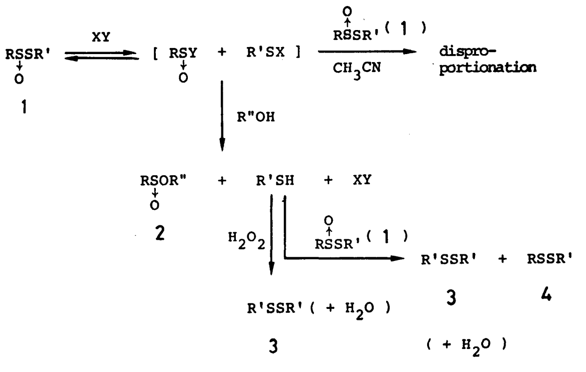
$$\mathbf{1} \xrightarrow[\substack{R''OH, r.t.,\\ <2\,h}]{Cat.(XY), H_2O_2} \mathbf{2} + \mathbf{3} \qquad (2)$$

These observations in addition to the previous results[2] seem to indicate that the reaction involves incipient formation of sulfinyl halide (RS(O)Y) which is derived by the reaction with the catalyst (XY), as shown in Scheme 1. The resulting mixture of RS(O)Y and R'SX then would react much more readily with a large excess of alcohol than with **1** to afford **2** and thiol (R'SH) which is capable of reducing **1** to give two disulfides (**3** and **4**).[3] However, in the *presence* of H_2O_2 R'SH is quickly oxidized to R'SSR' which no longer has the reducing ability. Therefore, the increase of

Table 1. Reactions of thiosulfinic *S*-ester (thiolsulfinate) with alcohol in the presence of catalyst[a)]

Entry No.	Substrate (RS(O)SR') R=	R'=	Alcohol (ml) R''OH R''=	Catalyst (mg)	Temp/°C	30% H_2O_2 (equiv.)[b)]	Yield/mol%[c)] 2	3	4	d)
1	*p*-Tol	Ph	Me 5	I_2 2.5	20	0	61	38	25	7.5
2	*p*-Tol	Ph	Me 10	I_2 2.5	20	0	66	40	21	6.6
3	*p*-Tol	Ph	Me 15	I_2 2.5	20	0	66	40	21	6.3
4	*p*-Tol	Ph	Et 5	I_2 2.5	20	0	69	40	20	5.2
5	*p*-Tol	Ph	*i*-Pr 5	I_2 2.5	20	0	69	39	19	5.7
6	*p*-Tol	Ph	Me 15	I_2 2.5	4	0	81	42	17	2.3
7	*p*-Tol	Ph	Me 10	36%HCl 30	20	0	70	38	24	4.2
8	*p*-Tol	Ph	Me 10	98%H_2SO_4 44	20	0	No reaction			
9	*p*-Tol	Ph	Me 10	70%$HClO_4$ 45	20	0	No reaction			
10	Ph	Ph	Me 10	Br_2 3.5	22	1.0	91	e)	0	Trace
11	Et	Et	*i*-Pr 10	Br_2 3.5	22	1.0	45	f)	0	25
12	*p*-Tol	Ph	Me 15	I_2 2.5	20	1.0	92	46	8.0	0
13	Ph	*p*-Tol	Me 10	I_2 4.6	18	1.0	88	40	10	Trace
14	Ph	Et	Me 10	I_2 4.6	18	1.0	90	45	7.0	0

a) Thiolsulfinate (*ca.* 1 mmol) was used as a substrate and the procedure is shown in Experimental section. b) The amount of 30% H_2O_2 is based on that of the substrate. c) Yields are determined on the basis of the amount of the substrate. d) A disproportionation product, $RS(O)_2SR$, was also obtained. e) Not determined. f) The yield could not be determined.



Scheme 1.

the yield of **2** by addition of H_2O_2[4] can be attributed to the decrease of the reductant R'SH, by the oxidation of R'SH to the unreactive disulfide (R'SSR') with H_2O_2.

The disproportionation rate of **1** in CH_3CN in the presence of halogen or hydrogen halide (XY) was faster than the rate of the formation of **2** in alcohol in the presence of both XY and H_2O_2. However, the disproportionation hardly occured in alcohol in which the formation of **2** must predominate over the disproportionation. Namely, the amount of alcohol used was in large excess so that RS(O)Y reacts much more easily with alcohol to form **2** than with **1** to disproportionate. The amount of solvent alcohol did not affect the yield of **2** (entries 1—3) and therefore, it is not necessary to use a very large amount of the alcohol.

This scheme is in good accordance with the data shown in Table in which the yield of **2** was rarely affected by the change of the bulkiness of alcohols used. This result is quite different from that in the oxidation of **1** with $NaIO_4$ in aqueous alcohol,[2] and it may be explained by assuming that RS(O)Y reacts only with the alcohol. Meanwhile, other catalysts such as H_2SO_4 and $HClO_4$ were found not to be effective enough to catalyze the reaction (entries 8 and 9), suggesting that RS(O)Y cannot be formed by the interaction with such catalysts in which the counter anions possess very little nucleophilicity. At lower temperatures, the reaction of RS(O)Y with alcohol to the sulfinate may slightly predominate over that with **1** to form the disproportionation products (entry 6). Change of the amount of H_2O_2 added (1—10 equiv.) did affect little the yield of **2** in the reaction of *S-p*-tolyl benzenethiosulfinate in EtOH. Similarly, the change of the amount of iodine (2.5—12.5%) as a catalyst also affected rarely the yield of **2** while the reaction time was shortened with increase of the amount of iodine. Iodine may be a better catalyst than HCl because of its easy handling and product selectivity. With hydrochloric acid the solution becomes acidic and may promote both the hydrolysis of the sulfinate formed with water present and the oxidation with H_2O_2.[4]

Thus, a new route of transformation of unstable thiolsulfinate to stable sulfinate has been found and is expected to be used as a facile method.

Experimental

General Procedure for Conversion of Thiosulfinic S-*Ester to Sulfinic Ester*: To an alcohol solution (10 ml) of thiosulfinic *S*-ester (*ca.* 1.0 mmol) in a 30 ml Erlenmeyer flask, 30% H_2O_2 (*ca.* 1.0 mmol) and 2.5 mg of solid iodine were added to initiate the reaction. The mixture was stirred at r.t. for 1—2 h. An aliquot of the reaction mixture was withdrawn and injected to GLC to determine the yields of the products. The structures and the yields of the products were also confirmed by NMR spectra of organic layer which was obtained by extracting the reaction mixture with $CHCl_3$, followed by usual work-up. The sulfinates thus obtained were identified by comparison of their retention times in GLC charts and then NMR spectra with those of the authentic samples prepared independently.[5,6] Purification of the sulfinate was carried out by column chromatography in which the residue after evaporation of $CHCl_3$ of the organic extract was eluted on silica gel by using hexane and then benzene or benzene as a sole solvent. The first fraction was a mixture of disulfides and the second was the sulfinate.

All thiosulfinic *S*-esters were prepared by the reported method.[7,8] S-*Phenyl Benzenethiosulfinate*: mp 69—70 °C (lit,[7] 69—70 °C), S-p-*Tolyl Benzenethiosulfinate*: mp 52 °C (lit,[7] 54 °C), S-*Phenyl* p-*Toluenethiosulfinate*: mp 78—80 °C (lit,[7] 76 °C), S-*Ethyl Benzenethiosulfinate*:[9] Colorless oil, NMR (δ, $CDCl_3$) 1.44 (t, 3H, CH_3, J=7.1 Hz), 3.13 (q, 1H, H_A or H_B of CH_2, J=7.1 Hz), 3.16 (q, 1H, H_B or H_A, J=7.1 Hz), 7.38—7.80 (m, 5H, arom); IR (neat, cm^{-1}) 3050, 2970, 2920, 1575, 1473, 1440, 1085 (S=O).

Authentic sulfinates were all known and prepared by the reactions of sulfinyl chlorides and excess alcohols.[5,6] Physical and spectroscopic data of these sulfinates were well consistent with their structures.

References

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