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SHORT COMMUNICATIONS

Efficient Oxidation of Sulfides to Sulfoxides and of Thiols to Disulfides with Aqueous HIO_3*

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Oxidations of thiols to disulfides and of sulfides to sulfoxides under mild conditions in organic media are of practical importance for organic synthesis. Taking into account that thiols and sulfides are easily oxidizable and may thus be overoxidized, extensive studies have been carried out to develop methods for controlled oxidation of these compounds [1–12]. The known oxidants are not free from disadvantages, including difficult accessibility [4, 8], methods of preparation [2, 8], long reaction time [5, 12], laborious treatment of the reaction mixture [4, 12], and high toxicity [1].

We have found that aqueous HIO_3 may be very effective reagent for the transformation of thiols into disulfides, ensuring high yields of the products and requiring no organic solvent (Table 1). Aqueous HIO_3 was also found to effectively oxidize sulfides to the corresponding sulfoxides. These reactions are carried out by heating the reactants on a steam bath, and sulfoxides are formed in excellent yields (Table 1). It should be noted that thiols and sulfides having double C=C bonds could not be oxidized with aqueous HIO_3 with the same selectivity; therefore, this procedure cannot be recommended for oxidation of unsaturated thiols and sulfides. Table 2 compares the efficiency of the proposed procedure with some published results [7, 8, 11]. The oxidation of sulfides and thiols with aqueous HIO_3 is superior to the other methods, for it utilizes cheap and accessible reagents, occurs under mild conditions, and ensures good yields and easy isolation of the products.

A mixture of 1 mmol of thiol or sulfide and 0.25 g of aqueous HIO_3 (54 wt %) was agitated at room temperature using a magnetic stirrer or heated on a steam bath for a time specified in Table 1. The progress of the reaction was monitored by TLC or GLC. When the reaction was complete, 5 ml of CH_2Cl_2 and 0.5 g of $Na_2S_2O_3$ were added, and the mixture was stirred for 15 min and filtered. The filtrate was dried over anhydrous $MgSO_4$ and evaporated, and the residue was purified by column chromatography on silica gel.

Reagents from Merck, Fluka, BDH, and Aldrich were used. The products were isolated and purified by chromatographic methods and were identified by comparing their physical properties (melting or boiling points and refractive indices) and IR and

Table 1. Oxidation of thiols to disulfides[a] and of sulfides to sulfoxides[b] with aqueous HIO_3

Substrate	Product	Time, min	Yield, %
PhSH	$(PhS)_2$	5	95
4-MeC_6H_4SH	$(4\text{-}MeC_6H_4S)_2$	5	90
4-ClC_6H_4SH	$(4\text{-}ClC_6H_4S)_2$	5	89
$PhCH_2SH$	$(PhCH_2S)_2$	15	95
C_4H_9SH	$(C_4H_9S)_2$	15	92
$HSCH_2CH_2CH_2SH$	–	15	–[c]
PhSMe	PhS(O)Me	15	95
PhSPh	Ph_2SO	30	92
$(PhCH_2)_2S$	$(PhCH_2)_2SO$	120	92
$(C_4H_9)_2S$	$(C_4H_9)_2SO$	60	87

[a] At room temperature.

[b] On heating on a steam bath.

[c] Polymerization of the substrate occurred.

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Table 2. Oxidation of benzenethiol and methyl phenyl sulfide with (*1*) aqueous HIO_3 (this work), (*2*) $Cu(NO_3)_2 \cdot 3H_2O$ [8], (*3*) MnO_2–HCl [11], and (*4*) pyridinium chlorochromate [13]

Substrate	Time, min (yield, %)			
	1	*2*	*3*	*4*
PhSH	5 (95)	10 (98)	–[a]	120 (82)
PhSMe	15 (95)	210 (85)	45 (99)	–[a]

[a] No reaction occurred.

NMR data with those of authentic samples. The purity of the products was checked by TLC on Polygram SILG/UV 254 plates or by GLC on a Shimadzu GC-14A chromatograph.

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