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# SODIUM CHLORITE - YET ANOTHER OXIDANT FOR THIOLS TO DISULPHIDES

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Dedicated to Professor T. R. Govindachari on the occasion of his 80th birthday.

**ABSTRACT**: An efficient oxidative coupling of thiols to disulphides is described using sodium chlorite which has good synthetic and commercial relevance.

The conversion of mercaptans to disulphides is an useful transformation and is of importance both from a biological and a practical point of view.<sup>(1)</sup>

The conversion is amply precedented in the literature. The reported reagents known to convert thiols to disulphides include Iodine-Hydrogen Iodide,<sup>(2)</sup> Thallium (111) acetate,<sup>(3)</sup> Bromine/aqueous Potassium hydrogen carbonate,<sup>(4)</sup> Nitric oxide and Nitrogen dioxide,<sup>(5)</sup> Barium permanganate under non-aqueous and aprotic conditions<sup>(6)</sup> and Ethyl dichlorophosphate.<sup>(7)</sup> A mild

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high yield conversion of a thiol to disulphide has been achieved recently using a disulphide dication salt.<sup>(8)</sup> Use of Sodium perborate<sup>(9)</sup> and Alkoxy stannateferric chloride<sup>(10)</sup> and Bakers' yeast for this transformation are also well documented.<sup>(11)</sup>. Sodium tellurite,<sup>(12)</sup> Zinc bismuthate<sup>(13)</sup> for disulphides have also been exploited. The aforementioned reagents suffer from either one or more of the following drawbacks such as availability of the reagent, preparation of the reagent, cumbersome work-up procedure, toxic or high cost rendering commercial exploitation impossible.<sup>(14)</sup>

Our interest in the disulphides arose from the need to commercialise a variety of fungitoxic compounds such as the thiuram disulphides and other heterocyclic disulphides which incidentally function as rubber accelerators such as MBTS (Dibenzothiaz-2-yl disulphide). Accordingly, our attention was focussed on evolving a viable technology for the production of fungicides containing air pollution and rendering effluent treatment easy.

Kageyama et al. observed oxidation of sulphides to sulphoxides by sodium bromite while claiming sodium chlorite to be a less attractive reagent for the purpose.<sup>(15)</sup> Sodium chlorite has been reported for oxidative conversion of aliphatic nitro compounds to carbonyl compounds<sup>(16)</sup>,  $\alpha$ , $\beta$ -unsaturated aldehyde to carboxylic acid<sup>(17)</sup> and in combination with H<sub>2</sub>O<sub>2</sub> and DMSO converts aldehydes to carboxylic acids.<sup>(18)</sup>

This led us to work out an attractive method under mild conditions using sodium chlorite for obtaining the desired disulphides. We subjected dialkyl dithiocarbamic acid or the sodium salt as the substrate which resulted in instantaneous formation of the tetraalkyl thiuram disulphides in very high yields and purity. This route eclipses the peroxide method generally adopted for the industrially useful disulphides quite a few of which display fungicidal properties.

By way of generalising the synthetic utility of the reagent as selective oxidant for thiols, the reagent was examined on a wide array of substrates such as aliphatic, aromatic thiols, heterocyclic dithiocarbamic acids and their sodium salts when we realised the formation of the corresponding disulphides in very high yields, purity and in highly diminished reaction times. Another noteworthy feature of the reagent lies in the exclusive formation of the disulphides irrespective of the presence of other oxidisable functions (-NH<sub>2</sub>, -OH, alkyl) present in some of the substrates studied. The reagent, however, did not furnish the expected products but led only to polymeric materials when reacted on certain dithiols (1,2-ethanedithiol, 1,3-propanedithiol, 2,5dimercapto, 1,3,4-thiadiazole). The synthetic utility and the mechanistic study of the transformation are under progress. Table (see) illustrates our findings.

#### EXPERIMENTAL SECTION

All reagents of laboratory grade were obtained and purified prior to use. Dithiocarbamic acids were prepared by reaction of carbon disulphide with the appropriate amine. Melting points were uncorrected. IR Spectra were recorded on a BRUCKER FTIR IFS-85 spectrometer. <sup>1</sup>H NMR spectra were obtained using HITACHI 60 MHz spectrometer. Mass spectra were taken in a SHIMAZDU GCMS Q.P-1000A (70 ev) mass spectrometer.

## TABLE: OXIDATION OF THIOLS AND DITHIOCARBAMIC ACIDS BY SODIUM CHLORITE

$\begin{array}{c} R \\ R \\ \hline \end{array} \begin{array}{c} N \\ R \\ \hline \end{array} \begin{array}{c} C \\ H \\ S \\ \end{array} \begin{array}{c} S \\ R \\ \end{array} \begin{array}{c} NaClO_2/H_2O \\ 0 - 5^{\circ}C, 20 \text{ min} \end{array} \begin{array}{c} R \\ R \\ R \\ \end{array} \begin{array}{c} N \\ R \\ \end{array} \begin{array}{c} C \\ -S \\ H \\ S \\ \end{array} \begin{array}{c} C \\ -S \\ -S \\ H \\ S \\ \end{array} \begin{array}{c} R \\ R \\ \end{array} \begin{array}{c} R \\ R \\ R \\ \end{array} \begin{array}{c} R \\ R \\ \end{array} \begin{array}{c} R \\ R \\ R \\ R \\ \end{array} \begin{array}{c} R \\ R \\ R \\ R \\ \end{array} \begin{array}{c} R \\ R \\ R \\ R \\ R \\ \end{array} \begin{array}{c} R \\ R \\ R \\ R \\ R \\ R \\ \end{array} \begin{array}{c} R \\ R $					
Sl. No.	R	Reaction Time (min)	Yield <sup>(a)</sup> (%)	Melting Point (°C)	
				Observed	Literature
1.	Methyl	20	93	150	151(19)
2.	Ethyl	20	92	68-70	70.5(19)
3.	Isopropyl	20	80	48-50	49-59(19)
4. <sup>(b)</sup>	Cyclohexyl	20	90	88-89	86-87(20)
5. <sup>(b)</sup>	Hydroxyethyl	20	73	57-59	61-63(21)
	R - SH	NaClO <sub>2</sub> /	H <sub>2</sub> O >	R-S-S-R	

0-5°c, 10-15 min

(6-12)

6.	2-Benzimidazolyl	15	95	200-202	198(22)
7.	2-Benzthiazolyl	15	97	180-182	182-183(23)
8.	2-Naphthyl	15	95	145	143-144(24)
9.	Phenyl	10	96	64-66	61-62(4)
10.	P-Tolyl	10	96	48	45-56(4)
11.	O-Aminophenyl	15	92	80	79-80(23)
12.	O-Carboxyl Phenyl	15	86	286	289-29027
13.	5-Amino 1,3,4 thiadiazolyl	15	90	235-238	239(25)

14.	Morpholinyl	15	94	147	149-150(26)
15.	Piperidinyl	15	93	78-80	78(27)
16.	Pyrrolyl	20	90	93-95	95-96 <sup>(28)</sup>
17.	Pyrrolidinyl	15	93	144-146	148(28)

a.

Yield of pure product Purified by silicagel column chromatography by cluting with hexane containing 2% ethylacetate. b.

## TYPICAL EXPERIMENTAL PROCEDURE

## Reaction of dithiocarbamic acid or thiol with sodium chlorite

To a stirred cold reaction mixture  $(0.5^{\circ}C)$  consisting of thiol or dithiocarbamic acid (0.01 M) in methanol (15ml), a sodium chlorite solution [0.0075 M, 0.678 g in water (20 ml)] for the thiol or [0.01 M, 0.904g in water (30 ml)] for the dithiocarbamic acid was added dropwise in 10 minutes. The resultant solution was stirred at 10°C for a further10 minute period. The solid obtained immediately was filtered and washed with water (2 x 25ml) and dried. In some cases extraction procedure was followed. The disulphide was isolated in excellent yields (73-97%). Hexane-chloroform was the preferred solvent mixture for crystallisation.

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