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Catalytic Oxidation of Mercaptans by Iodine-Hydrogen Iodide System in Dimethyl Sulfoxide

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Synopsis. Mercaptans were oxidized readily by a catalytic amount of iodine or hydrogen iodide (*i.e.*, aq. HI-solution) in the presence of dimethyl sulfoxide to afford the corresponding disulfides nearly quantitatively.

As reported previously,[1)] the reduction of sulfoxides, especially dialkyl sulfoxides (*e.g.*, dimethyl sulfoxide) was found to take place catalytically by either bromine or hydrogen bromide. The mechanism for this reaction was proposed to proceed *via* an initial bromination of the sulfoxide affording the corresponding α-bromo sulfoxide which then reacts with another sulfoxide regenerating the corresponding sulfide and hydrogen bromide (Kornblum Reaction).[2)] Meanwhile, hydrogen bromide is well known to reduce the sulfoxide to the corresponding sulfide.[3)] Thus, the whole process may form a kind of the Oxidation-Reduction Cycle by the bromine–hydrogen bromide system in the sulfoxide.

Therefore, if the above reaction system is treated with a third component which reacts with either bromine or hydrogen bromide, a new synthetic application of this system will be resulted.

Meanwhile, it is known that the oxidation of mercaptans proceeds in dimethyl sulfoxide (DMSO) solution, but the reaction requires high temperature and a prolonged reaction time.[4)] While, iodine (I_2) is a mild and convenient oxidizing reagent for the preparation of disulfides from the corresponding mercaptans,[5)] and the reaction is considered to proceed through the following reaction path.

$$\mathrm{RSH} + \mathrm{I_2} \longrightarrow \mathrm{RSI} + \mathrm{HI}$$

$$\mathrm{RSI} + \mathrm{RSH} \longrightarrow \mathrm{RSSR} + \mathrm{HI}$$

Thus, if iodine is regenerated from hydrogen iodide (HI), this oxidation may be carried out by the use of a small amount of iodine or hydrogen iodide under a mild condition. Actually, when the oxidation of mercaptan was carried out in DMSO with a catalytic amount of iodine (or hydrogen iodide), the oxidation proceeded nearly quantitatively at room temperature affording the corresponding disulfide. Therefore, our present method is to be a simple and convenient preparation of disulfides.

The oxidation of mercaptan by iodine or hydrogen iodide was carried out under various reaction conditions. The results obtained are summarized in Table 1.

Inspection of the data in Table 1 shows that the oxidation of mercaptan by iodine or hydrogen iodide took place only in the presence of DMSO (Runs 6 and 7), and gave a nearly equal amount of dimethyl sulfide (DMS) to that of the corresponding disulfide. These observations suggest clearly that the oxidation of mercaptan and the reduction of DMSO occur simultaneously. Namely, iodine undoubtedly initiates the oxidation of mercaptan affording disulfide and hydrogen iodide which is readily oxidized by DMSO to iodine. Therefore, iodine acts only as a catalyst for the present reaction.

In order to generalize this catalytic oxidation of mercaptan by iodine, various mercaptans were reacted in sealed tubes at room temperature. The results

TABLE 2. CATALYTIC PREPARATION OF DISULFIDE FROM MERCAPTAN BY IODINE
$\mathrm{RSH} + \mathrm{I_2}(1/100\ \mathrm{mol}\ \%\text{-RSH}) + \mathrm{DMSO}\ (\mathrm{excess})^{a)}$ in Benzene at Room Temperature for 5 h.

R	Products and yields$^{b)}$ (%)	
	RSSR	DMS
Et	97	93
n-Pr	94	95
i-Pr	92	96
n-Bu	97	95
t-Bu	43	38
Ph	98	94
p-Tol	95	92
p-ClC_6H_4	97	93

a) Six times excess to that of mercaptan used.
b) Although iodine was detected, the yield was not determined.

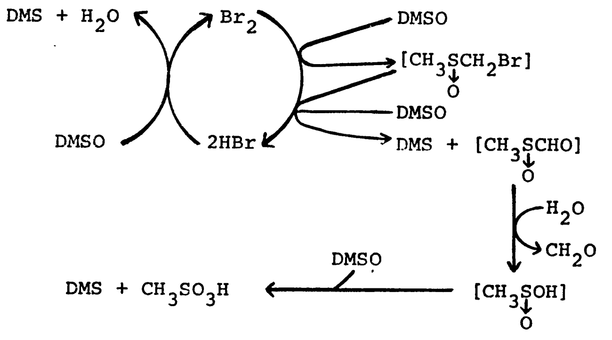
TABLE 1. OXIDATION OF BUTYL MERCAPTAN BY IODINE OR HYDROGEN IODIDE IN BENZENE

Run	I_2 or HI$^{a)}$ (mol %-SH)	DMSO	Reaction condition		Products (%)		
			Temp (°C)	Time (h)	$(n\text{-BuS})_2$	DMS	Other
1	I_2 (50)	—	r.t.	0.1	96	—	$I_2$$^{c)}$
2	I_2 (50)	excess$^{b)}$	r.t.	0.1	93	98	$I_2$$^{c)}$
3	HI (100)	—	r.t.	0.1	—	—	—
4	HI (100)	excess$^{b)}$	r.t.	0.1	97	95	$I_2$$^{c)}$
5	I_2 (1)	—	40	3.0	—	—	$I_2$$^{c)}$
6	I_2 (1)	excess$^{b)}$	40	3.0	97	98	$I_2$$^{c)}$
7	HI (2)	excess$^{b)}$	40	3.0	95	94	$I_2$$^{c)}$

a) Aqueous HI-solution (*ca.* 40%) was used. b) Six times excess to that of mercaptan used. c) Iodine was detected, but the yield was not determined.

obtained are listed in Table 2.

These results shown in Table 2 reveal clearly that this reaction is a facile method to prepare disulfide from the corresponding mercaptan, while the plausible reaction scheme may be depicted as shown in Scheme 1.



* DMS : Dimethyl Sulfide

Scheme 1.

Experimental

Materials. *Mercaptan*: Alkyl mercaptans and thiophenol were commercial products. *p*-Tolyl and *p*-chlorophenyl mercaptans were prepared from the corresponding sulfonyl chloride and zinc in sulfuric acid by a known method.[6]

Dimethyl sulfoxide: The commercial product was purified by usual method (dried over calcium hydride and then distilled).

Iodine and Hydrogen iodide: The commercial products (HI: *ca.* 40% aqueous solution) were used without further purification.

General Apparatus. GLPC analysis was performed with a Hitachi Gas Chromatography with a thermal conductivity detector, equipped with a 2 m × 3 mmϕ stainless steel column packed with Silicon GE SE-30 on 60—80 mesh Chromosorb W (AW). Preparative column chromatography was performed with silica gel (Wakogel C-200) using benzene-hexane as an eluent.

Product Analysis. The yield of the disulfides was determined only by GLPC measurement, and the yield after the isolation slightly decreased. Dialkyl disulfides were separated by GLPC and preparative column chromatography and diaryl disulfides were separated by preparative column chromatography, and identified by comparing their mp and spectroscopic analyses with those of the authentic samples.

Oxidation of Mercaptan by Iodine. A typical run was as follows: Butyl mercaptan (0.2 g; 2.2 mmol), iodine (0.006 g; 0.02 mmol) and DMSO (1.0 g; 12.8 mmol) were dissolved in 5 ml of benzene. The mixture was placed in a sealed tube, and was allowed to stand at room temperature for 3 h. Then, the sealed tube was broken and 5 μl of the reaction mixture was directly injected into a column of GLPC to determine the amount of dimethyl sulfide. The yield was 95%. To the rest of the reaction mixture, 10 ml of aq. NaOH (1/10 M) solution was added, and after shaking the mixture vigorously, the benzene layer was separated. From the benzene layer, dibutyl disulfide was isolated by GLPC and preparative column chromatography. The yield was 97%. Meanwhile, the colorless reaction mixture turned to red at the completion of the reaction, and the red color faded away upon treatment with sodium hydrogen sulfite. This suggests that iodine was present in the reaction mixture.

All the other reactions were carried out as described above.

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