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The Oxidation of Thiols to Disulfides with Manganic Tris (acetylacetonate)

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Various methods are available for oxidizing thiols to disulfides.[1] However, only a few procedures are available for the oxidation of thiols to disulfides, in the absence of oxygen, by means of metal salts, such as lead tetraacetate,[2] ferric octanonate,[3] cupric octanonate,[3] and transition metal oxides.[4] It has recently been reported that manganic tris (acetylacetonate) (MTA) in carbon disulfide or acetonitrile acts as a coupling agent for phenols.[5]

The present note will describe a successful extension of this method to oxidizing thiols, including alkyl, benzyl, and aryl, to the corresponding disulfides. Thus, 1-pentanethiol, α-toluenethiol, benzenethiol, and 2-napthalenethiol, were readily converted into *n*-pentyl disulfide,[6] benzyl disulfide,[2b] phenyl disulfide,[2b] and 2-naphthyl disulfide,[7] respectively. All the reactions were carried out in carbon disulfide under nitrogen at room temperature. The reaction conditions employed and the results obtained are summarized in Table 1. All the yields recorded in Table 1 are based on the amount of disulfide isolated. The advantages of this convenient method are that all the reactions proceed rapidly at room temperature and that all give virtually quantitative yields of the disulfides and no other highly-oxidized products. One mole of MTA was found to oxidize about one mole of thiol. During the reaction, there was formed a precipitate which had a manganous bis (acetylacetonate) as its main component.[5] Accordingly, the following equation for the reaction is appropriate:

TABLE 1. OXIDATION OF THIOLS TO DISULFIDES WITH MTA

Reactant	Thiol/ MTA[a]	Time (min)	Product	Mp or bp, °C(mmHg)		Yield[b] (%)
				Found	Reported	
1-Pentanethiol	1.05	90	*n*-Pentyl disulfide	110—113(4)	90—92(1)[6]	85
α-Toluenethiol	1.05	90	Benzyl disulfide	69—71	70—71[2b]	99
Benzenethiol	1.05	90	Phenyl disulfide	59	59—61[2b]	95
Benzenethiol	0.5	90	Phenyl disulfide			96
2-Naphthalenethiol	1.05	130	2-Naphthyl disulfide	140	138—9[7]	94

a) Molar ratio. b) Based on reacted MTA.

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[1] D. S. Tarbell, "Organic Sulfur Compounds," Vol. I, ed. by N. Kharasch, Pergamon Press, New York, N. Y. (1961), p. 97; A. A. Oswald and T. J. Wallace, "Organic Sulfur Compounds," Vol. II, ed. by N. Kharasch and C. Y. Meyers, Pergamon Press, New York, N. Y. (1966), p. 205.

[2] a) L. Suchomelová and J. Zy'ka, *J. Electroanal. Chem.*, **5**, 57 (1963); b) L. Field and J. E. Lawson, *J. Amer. Chem. Soc.*, **80**, 838 (1958).

[3] T. J. Wallace, *J. Org. Chem.*, **31**, 3071 (1966).

[4] T. J. Wallace, *ibid.*, **31**, 1217 (1966).

[5] M. J. S. Dewar and T. Nakaya, *J. Amer. Chem. Soc.*, **90**, 7134 (1968).

[6] E. Miller, F. S. Crossley and M. L. Moose, *ibid.*, **64**, 2322 (1942).

[7] V. N. Belov and M. Z. Finkel'shtein, *J. Gen. Chem.* (*U. S. S. R.*) **17**, 741 (1947); *Chem. Abstr.*, **42**, 1238 (1948).

TABLE 2. ATTEMPTED ADDITION REACTIONS OF 1-DODECANETHIOL TO 1-DODECENE CATALYZED BY MTA[a)]

1-$C_{12}H_{25}SH$, mol	MTA, mol	1-$C_{12}H_{25}SH$/MTA[b)]	1-Dodecene/1-$C_{12}H_{25}SH$[b)]	Time, hr	% conversion of 1-$C_{12}H_{25}SH$	Dodecyl disulfide, mol	Dodecyl sulfide, mol
0.01	0.01	1	3.5	20	~100	5.0×10^{-3}	None
0.01	0.002	5	3.5	20	20	1.0×10^{-3}	None

a) All reactions were carried out in 50 m*l* of xylene under nitrogen at room temperature.
b) Molar ratio.

$$2RSH + 2Mn(Acac)_3 \longrightarrow RSSR + 2Mn(Acac)_2 + 2AcacH$$

As can be seen from Table 1, about one mole of MTA was consumed per mole of benzenethiol, when a one-molar excess of MTA was present. These results suggest that MTA in carbon disulfide acts as a specific oxidant for the oxidation of thiols.

For the oxidation of thiols to disulfides by ferric octanonate, Wallace[3)] proposed the following mechanism (the radical nature of the reactions was established by trapping the thiyl radical with 1-dodecene):

$$RSH + Fe(Oct)_3 \longrightarrow RS\cdot + Fe(Oct)_2 + OctH$$

$$RS\cdot \longrightarrow \tfrac{1}{2}RSSR$$

In order to obtain information regarding the nature of the oxidation of thiols to disulfides by MTA, the addition reactions of 1-dodecanethiol to 1-dodecene catalyzed by MTA were attempted in xylene according to the procedure of Wallace.[3)] The results are shown in Table 2. In contrast to the results obtained by Wallace, however, no dodecyl sulfide was detected; dodecyl disulfide was the only product. The fact that no dodecyl sulfide was formed may be explained by the following reaction scheme, involving thioxynium ion as an intermediate:[8)]

$$RSH + Mn(Acac)_3 \longrightarrow RS\cdot + Mn(Acac)_2 + AcacH$$

$$RS\cdot + Mn(Acac)_3 \xrightarrow{\text{fast}} RS^+ + Mn(Acac)_2 + Acac^-$$

$$RS^+ + RSH \longrightarrow RSSR + H^+$$

In the above reaction scheme it is assumed that MTA rapidly oxidizes the thiyl radical to the corresponding thioxynium ion because the oxidizing agent[5)] is more powerful than ferric octanonate.

Experimental

Materials. The 1-pentanethiol, α-toluenethiol, benzenethiol, 2-naphthalenethiol, 1-dodecanethiol, 1-dodecene, and cetane were commercial materials and were purified by crystallization or distillation. The MTA was prepared according to the method of Charles.[9)]

General Procedure for the Oxidation of Thiols to Disulfides. The following is the general procedure by which the disulfides listed in Table 1 were prepared. Into a solution of 15.8 mmol of the required thiol in 20 m*l* of carbon disulfide, we stirred, drop by drop and under nitrogen, a solution of 15 mmol of MTA in 250 m*l* of carbon disulfide. After a while, a pale yellow crystalline solid began to separate from the solution. After the reaction mixture had been vigorously stirred at room temperature for 1 hr, the solvent was evaporated to dryness under reduced pressure. The residue was extracted twice with 100 m*l* of petroleum ether (bp 30—60°C). The insoluble material was then filtered off and washed with 30 m*l* of petroleum ether. The combined filtrate was cautiously evaporated under reduced pressure to give the crude disulfide. With the exception of *n*-pentyl disulfide, which was distilled under reduced pressure, the products were recrystallized from petroleum ether.

The elemental analyses of the products were satisfactory, and the IR and NMR spectra were consistent with the proposed structures.

The Attempted Addition Reactions of 1-Dodecanethiol to 1-Dodecene Catalyzed by MTA. The procedures were identical with those reported by Wallace.[3)] For the analyses of the reactions, a Yanagimoto Model GCG-550-FP-type gas chromatograph was used.

[8)] L. S. Levitt, *Can. J. Chem.*, **31**, 915 (1953).

[9)] R. G. Charles "Inorganic Syntheses," Vol. VII, ed. by J. Kleinberg, McGraw-Hill Company, New York, N. Y. (1963), p. 183.