[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STEVENS INSTITUTE OF TECHNOLOGY]

Preparation of Alkyl Thiolsulfinates, Thiolsulfonates, and α-Disulfones[1]

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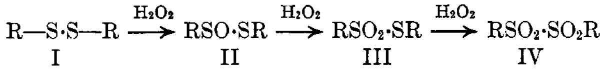
The sulfur atoms of disulfides take on in stepwise manner one, two or four atoms of oxygen when treated with hydrogen peroxide. Thiolsulfinates with large alkyl groups are stable in high vacuum and on long standing.

Low molecular weight alkyl thiolsulfinates have been made by the oxidation of disulfides[2] with peracetic acid and by the reaction between sulfinyl chlorides and mercaptans.[3] They are oils which decompose on standing[2,3]; aromatic thiolsulfinates decompose when subjected to high vacuum or intensive drying.[4]

Thiolsulfonates have been made in various ways from disulfides,[5] thiolsulfinates[6] and sulfinic acids.[7] They do not decompose on standing. Only methyl methanethiolsulfonate has been made by direct action of hydrogen peroxide on the corresponding disulfide.[3]

The α-disulfones, of both small and large alkyl groups, are stable solids prepared by the permanganate oxidation of sulfinic acids.[8] They result in small amount from the treatment of disulfides by ozone[5a]; the ethyl derivative has been made by peroxide treatment of the disulfide.[9]

It has been found that the stepwise oxidation of disulfides by 30% hydrogen peroxide takes place readily and can be used to prepare the three classes of compounds.



$$\underset{\text{I}}{\text{R—S·S—R}} \xrightarrow{H_2O_2} \underset{\text{II}}{\text{RSO·SR}} \xrightarrow{H_2O_2} \underset{\text{III}}{\text{RSO}_2\text{·SR}} \xrightarrow{H_2O_2} \underset{\text{IV}}{\text{RSO}_2\text{·SO}_2\text{R}}$$

The trioxide, $RSO_2.SOR$, was not found although it has been assumed,[10] but not isolated, as a product of oxidation of aromatic disulfides by hydrogen peroxide in alcohol.

When R is an undecyl or higher group, the thiolsulfinates are solids, stable in high vacuum or on standing and do not decompose on recrystallization. The atomatic thiolsulfinates, phenyl and *p*-tolyl, decompose to some extent during recrystallization and are more difficult to purify than the aliphatic compounds.

Gilman, Smith, and Parker[11] made *p*-tolyl disulfone by oxidizing the thiolsulfonate with peroxide but did not report a yield. On repeating their work we were able to get only about 7% of disulfone; use of peracetic acid gave a 10% yield. This contrasts with 22% and 37% yields of dodecyl disulfone from hydrogen peroxide and peracetic acid oxidations of 1-dodecyl 1-dodecanethiolsulfonate. Apparently the sulfur-sulfur bond is more stable when the attached groups are aliphatic than when they are aromatic.

EXPERIMENTAL

Aliphatic disulfides. These were made in the usual way by peroxide oxidation of mercaptan in alkaline solution.

The reactions of the dodecyl compounds may be considered typical.

1-Dodecyl 1-dodecanethiolsulfinate. To a solution of 5 g. of *n*-dodecyl disulfide in 500 ml. of acetic acid at 40–45° was added dropwise 3.25 g. (100% excess) of 27.1% hydrogen peroxide; there was no rise in temperature. The mixture was allowed to stand for one day at room temperature and then poured into water. After about a day the solid was removed by filtration, dried in the air and dissolved in petroleum ether. On cooling to 5°, a white solid separated and was recrystallized from alcohol, 4.3 g. (80% yield), m.p. 53°, soluble in chloroform, benzene and acetic acid; 0.5 g. of thiolsulfonate was also obtained. A higher temperature or longer period of standing will cause the formation of a larger quantity of the by-product thiolsulfonate.

1-Dodecyl 1-dodecanethiolsulfonate[12]. A. About 100% excess of 34.5% hydrogen peroxide was added to a solution of 0.1 g. of dodecyl dodecanethiolsulfinate in 40 ml. of acetic acid at room temperature. After 4 days the solution was poured into water, salt added and, after a few hours, the suspension filtered. The dried filter paper was extracted with benzene; evaporation of the benzene left 0.08 g. (77% yield) of thiolsulfonate.

B. Thiolsulfonate may be made directly from a disulfide by letting it stand 4 days with 120% excess of peroxide. From 0.5 g. of dodecyl disulfide the yield was 0.215 g. (39.8%).

C. Peracetic acid, 10–15% excess, oxidized thiolsulfinate and disulfide to thiolsulfonate, giving 47.7% and 57.1% yields respectively.

p-Tolyl disulfone. The earlier work[11] was repeated, using 0.1 g. (0.36 mmole) of *p*-tolyl thiolsulfonate. Crystals of

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(1) Supported in part by the Public Health Service, National Institutes of Health, Grant A-3649(Cl).

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(3) H. J. Backer and H. Kloosterziel, *Rec. trav. chim.*, **73**, 129 (1954).

(4) D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(5) (a) D. Barnard, *J. Chem. Soc.*, 4547 (1957); (b) H. J. Backer, *Rec. trav. chim.*, **67**, 894 (1948); (c) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **24**, 973 (1959).

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(7) For references see P. Allen, Jr. and L. Reich, *J. Phys. Chem.*, **64**, 1928 (1960).

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(9) A. Baroni, *Atti accad. Lincei*, **11**, 907 (1930).

(10) U. Marangelli, G. Modena, and P. E. Todesco, *Gazz. chim. ital.*, **90**, 681 (1960).

(11) H. H. Gilman, L. H. Smith, and H. H. Parker, *J. Am. Chem. Soc.*, **47**, 851 (1925).

(12) See also ref. 6 and 9.

TABLE I

R	M.P.	RSO·SR, % S Calcd.	RSO·SR, % S Found	M.P.	RSO_2·SR, % S Calcd.	RSO_2·SR, % S Found
n-C_{11}	52–53	16.41	16.04[a]	39–39.5	15.77	16.08
n-C_{12}	53	15.31 (Calcd. C, 68.90; H, 12.03.	15.52[b] Found C, 68.91; H, 12.11)[b]	(43.5–44)		
n-C_{14}	62–62.5	13.50	13.53	53–53.5	13.06	13.05[a]
n-C_{16}	69–70	12.08	12.08	59–60	11.72	11.71

[a] Microanalysis by Alfred Bernhardt, Max-Planck Institute, Mülheim (Ruhr), Germany. [b] Microanalysis by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

disulfone were obtained, 0.005 g., m.p. 218–220° and 0.004 g. of lower melting solid, approximately 7–8% yield.

1-Dodecyl disulfone. A. With 0.156 g. (0.36 mmole) of dodecyl dodecanethiolsulfonate and the same quantities of reagents as used with p-tolyl thiolsulfonate, solid formed in a few minutes. More acetic acid was added; after two days the solid was filtered off, and recrystallized from ethanol; yield 0.037 g. (22%) of disulfone.

B. A solution of 0.3 g. of dodecyl thiolsulfonate in 20 ml. of acetic acid and 500% excess 34.5% hydrogen peroxide was kept at 50–55° for 2.5 hr. After standing about a day, the mixture had crystals of disulfone, m.p. 100°, yield 0.083 g. (26%). Replacing the peroxide by peracetic acid raised the yield to 37%.

C. Direct oxidation of dodecyl disulfide by 500% excess hydrogen peroxide for 2.5 hr. at 50–55° gave 10–13% of disulfone; 0.3 g. of disulfide in 30 ml. of acetic acid and 500% excess peracetic acid warmed at 50–55° for 2.5 hr. yielded 0.055 g. (16%) of disulfone.

Stability of thiolsulfinates. Undecyl, tetradecyl and hexadecyl thiolsulfinates were kept at a pressure of 10^{-4} mm. for 48 hr. at room temperature; dodecyl thiolsulfinate was kept at 10^{-6} mm. for 36 hr. There was no change in melting point or appearance of any of the samples. Dodecyl thiolsulfinate did not change in melting point on standing 18 months in the laboratory in a stoppered vial.

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A New Preparation of Some Dimethylamino Derivatives of Boron

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The reaction of $Al[N(CH_3)_2]_3$ with the following types of boron compounds, R_3B, $(RBO)_3$, $(RO)_3B$ and $RBH_2·N(CH_3)_3$ was found to produce the dimethylamino derivatives; $R_2BN(CH_3)_2$ $RB[N(CH_3)_2]_2$, $B[N(CH_3)_2]_3$, and $RBNH(CH_3)_2$, respectively.

The dialkylaminoboranes have recently been the subject of several investigations. Niedenzu and Dawson[1,2] synthesized numerous derivatives of the type R_2BNR_2 by the reaction of a dialkylaminodichloroborane or a dialkylaminochlorophenylborane derivative with a suitable Grignard reagent. The dialkylaminodialkylboranes were also recently studied by Coates and Livingstone.[3]

Only a few examples of another class of aminoboranes, the bis-dialkylaminoalkylboranes, are known.[4] Hawthorne obtained bis-diethylamino-n-butylborane from the reaction of diethylamine with trimethylamine-n-butylborane. However, it was not possible to prepare the corresponding s-butyl- and t-butyl derivatives by this method. Instead, derivatives of the type $RBHN(C_2H_5)_2$ were obtained.

The observation that dimethylaminoboron dichloride was produced in the reaction between boron trichloride and trisdimethylaminoalane[5] suggested that other boron compounds might undergo a similar exchange reaction. It was found that by reaction of the appropriate boron compound with trisdimethylaminoalane, dimethylaminoalkylborane derivatives of the following types $R_2BN(CH_3)_2$, $RBHN(CH_3)_2$, $RB[N(CH_3)_2]_2$, and $B[N(CH_3)_2]_3$ could be prepared.

RESULTS

The reaction between trisdimethylaminoalane and boron trichloride[5] was extended to other simple boron compounds in order to determine the scope of the reaction. The compounds investigated may be divided into three general classes: the trialkylboranes or triarylboranes, boron compounds containing an oxygen-boron linkage and trimethyl-

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(2) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4225 (1960).

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