

bromide, BuSCHBrCH_3 , which, according to Markownikow's rule,¹ would be expected. To test this conclusion, the product was made to react with the sodium compound of butyl mercaptan as described above. A bis-sulfide was obtained, which boiled at $106-7^\circ$ at 3 mm. This, on oxidation, gave a sulfone melting at 180° which is known to be $\text{BuSO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Bu}$, instead of the sulfone $(\text{BuSO}_2)_2\text{CHCH}_3$ which melts at 64° . This showed that hydrobromic acid had added to regenerate some at least of the original primary bromide. Since the yields of these sulfones are always low, the presence of some of the isomeric bromide is not excluded.

The Iodide.—An attempt was made to obtain this compound by allowing a mixture of 15 g. of the chloride, 20 g. of sodium iodide and 80 cc. of alcohol to stand during the night. Water caused the formation of an oily layer which was washed, and dried over calcium chloride. This liquid contained 41.89% of iodine instead of 52.02% calculated for the iodide. An attempt was made to distil it *in vacuo*, but decomposition took place accompanied by deposition of iodine on the sides of the flask. A viscous oil was left as a residue. This was washed with a solution of thiosulfate and the iodine in the residual oil was determined. The iodine content was found to be 76.33%, which agrees with 76.48% calculated for $\text{C}_4\text{H}_9\text{SI}_2\text{CH}_2\text{CH}_2\text{I}$, though this agreement is regarded as largely accidental in view of the properties of the residue. Rathke² has prepared an analogous compound, $(\text{C}_2\text{H}_5)_2\text{SI}_2$.¹

The peculiar difficulty encountered with the iodide may be related to the known tendency of sulfides to form sulfonium compounds with alkyl iodides. A complicated sulfone might be formed by the union of the iodide with itself. This would be decomposed by heat, and liberated iodine might combine with some of the iodide.

Summary.

The following compounds have been prepared: *n*- $\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{OH}$, butyl mercapto-ethyl alcohol; *n*- $\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{OCOCH}_3$, butyl mercapto-ethyl acetate; *n*- $\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{Cl}$, butyl mercapto-ethyl chloride; *n*- $\text{C}_4\text{H}_7\text{-SCH}_2\text{CH}_2\text{Br}$, butyl mercapto-ethyl bromide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

SOME DERIVATIVES OF BUTYL MERCAPTAN AND THEIR MERCURIC IODIDE COMPOUNDS.³

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Most of the investigations concerned with mercaptans have been limited almost exclusively to the lower members of the series, *viz.*, to methyl and ethyl mercaptans. The following investigation was undertaken to extend our knowledge to the higher members of the series, particularly to normal butyl mercaptan and to accumulate further information about compounds which contain the sulfide grouping more than once, or this group with other groups.

¹ *Ber.*, **2**, 660 (1869); *Ann.*, **153**, 256 (1870).

² Rathke, *Ann.*, **152**, 214 (1869).

³ This and the preceding article are taken from the Doctor's dissertation of Thomas Cobb Whitner, Jr.

The work may be divided into 2 parts: compounds prepared by the action of the sodium salt of butyl mercaptan with halides; and those prepared from butyl mercaptan with aldehydes or ketones.

The sulfones of these sulfides, as well as their mercuric iodide compounds, have been prepared, partly for their own sakes and partly to furnish solids for identification and for analysis.

Experimental.

Reactions with Halides.

The mercaptan was dissolved in from 3 to 5 parts of 95% alcohol, together with an equivalent amount of sodium hydroxide, and to this mixture the calculated amount of the halide was added. The mixture was heated till the reaction seemed to be complete, diluted with water, and the oil separated. From the less volatile oils, impurities were eliminated by steam distillation. The oils were dried over calcium chloride and fractioned, usually *in vacuo*. It is hard to give yields on account of distillation losses, but they were all fairly good. The halides used were ethyl iodide, methylene chloride, ethylene bromide, chloro-methylethyl ether and phenacyl chloride. The following compounds have been prepared: ethylbutyl sulfide; methylene dibutyl sulfide or dibutyl mercapto-methane; ethylene dibutyl sulfide or α,β -dibutyl mercapto-ethane; ethoxy-methyl-butyl sulfide; and butyl phenacyl sulfide. Their properties are given in Table I.

TABLE I.

Formula.	B. p. ° C.	d_0^0 .	d_{25}^{25} .	n_D^{20} .
$C_7H_{15}SC_4H_9$	144-5	0.8763	0.8574	1.6527
$C_4H_9SCH_2SC_4H_9$	146 at 43 mm.	0.9482	0.9332	1.4964
$C_4H_9SCH_2CH_2SC_4H_9$	129-30 at 5 mm.	0.9524	0.9389	1.4962
$C_2H_5OCH_2SC_4H_9$	179-81	0.9054	0.8877	1.4502
$C_6H_5COCH_2SC_4H_9$	140 at 5 mm.	1.0712	1.0589	1.5050

Reactions with Aldehyde and with Ketones.

The reactions of butyl mercaptan with aldehydes and with ketones were all carried out under the same conditions. The aldehyde, or ketone, was mixed with 2 equivalents of the mercaptan and the mixture heated to 50-60° under a reflux condenser for several hours, while a slow current of dry hydrogen chloride was passed into the liquid. With acetaldehyde, application of heat was not required. Water was added to the product, which was then distilled with steam to rid it of volatile impurities. The residual oil was separated, dried over calcium chloride and fractioned *in vacuo*. The yields of purified products were 50 to 60% of the calculated amounts. The following compounds have been prepared: acetaldehyde-dibutyl mercaptal; acetone-dibutyl mercaptal; benzaldehyde-dibutyl mercaptol; and acetophenone dibutyl mercaptol. Their physical properties are given in Table II.

TABLE II.

Formula.	B. p. ° C.	d_0^0 .	d_{25}^{25} .	n_D^{20} .
$\text{CH}_3\text{CH}(\text{SC}_4\text{H}_9)_2$	105 at 3 mm.	0.9399	0.9272	1.4900
$(\text{CH}_3)_2\text{C}(\text{SC}_4\text{H}_9)_2$	110 at 4 mm.	0.9304	0.9215	1.4842
$\text{C}_6\text{H}_5\text{CH}(\text{SC}_4\text{H}_9)_2$	167 at 4 mm.	1.0180	0.9999	1.4445
$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{SC}_4\text{H}_9)_2$	167-8 at 3 mm.	1.0241	1.0110	1.5535

Sulfones.

Dibutyl Sulfone Methane, $\text{C}_4\text{H}_9\text{SO}_2\text{CH}_2\text{SO}_2\text{C}_4\text{H}_9$.—Various methods of oxidation were tried, but none was found entirely satisfactory; the yields were generally poor.

Four g. methylene dibutyl sulfide was added to 150 cc. of water containing 16 cc. of sulfuric acid and 25 g. of sodium dichromate. A vigorous reaction took place, after which the mixture was boiled for 45 minutes. As the liquid cooled, the sulfone separated. After recrystallization from hot water, it formed large white plates. The same product was obtained when 5 g. of the sulfide was dropped into 20 cc. of fuming nitric acid. The sulfone separates when this mixture is poured into water. The yield was about 2 g. by each method. The melting point is 182° .

Calc.: S, 25.03. Found: 25.06.

Ethylene Dibutyl Sulfone, $\text{C}_4\text{H}_9\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_4\text{H}_9$.—Ten cc. of the sulfide was added slowly to 20 cc. of fuming nitric acid, while the acid was cooled and stirred. When this product was poured into water, 25 g. of the sulfone separated. Recrystallized from hot water, it melted at 180° .

Calc.: S, 23.73. Found: 23.65.

Ethylidene Dibutyl Sulfone, $\text{CH}_3\text{CH}(\text{SO}_2\text{C}_4\text{H}_9)_2$.—While a suspension of 5 g. of the sulfide in 300 cc. of 2% sulfuric acid was stirred rapidly, a 5% solution of potassium permanganate was added to it slowly till the pink color was permanent; then sodium sulfite was added to dissolve manganese dioxide. The solution was evaporated to $\frac{1}{3}$ its volume, filtered and cooled. This caused the separation of the sulfone as white needles. It melts at 64° .

Calc.: S, 23.73. Found: 23.97.

Benzylidene Dibutyl Sulfone, $\text{C}_6\text{H}_5\text{CH}(\text{SO}_2\text{C}_4\text{H}_9)_2$, was prepared by the same method. Yield, 0.2 g. from 5 g. of sulfide; m. p., 86° . A better yield (0.4 g. from 3 g.) is obtained if a solution of the sulfide in 60 cc. of acetic acid is treated first with water until an incipient turbidity appears, and then slowly with pulverized permanganate. Occasionally some dil. sulfuric acid should be added. When the calculated amount of permanganate had been used the solution was diluted with 100 cc. of water, cooled and filtered. The precipitate was extracted with boiling water from which the sulfone crystallized as white needles. This is a modification of the method employed by Hilditch.¹ No sulfones could be obtained from

¹ Hilditch, *J. Chem. Soc.*, 93, 1524 (1908).

the mercaptols made with acetone and with acetophenone; oxidation to sulfonic acids must have taken place. When the sulfur atoms are separated by 2 carbon atoms, $\text{RSCH}_2\text{CH}_2\text{SR}'$, strong oxidizing agents may be used.

Though all of the oxidation methods mentioned above were tried sulfones were not obtained from ethoxy-methyl-butyl sulfide, acetone-dibutyl mercaptal and acetophenone dibutyl mercaptol.

Mercuric Iodide Derivatives.

It was expected that mercuric iodide would combine with these sulfides 1:1, but, except for the 2 sulfides, methylene dibutyl sulfide and ethylene dibutyl sulfide, this was found not to be the case. In all other cases the ratio of iodine to mercury in the product was less than 2:1, which implies that combination takes place with mercuric rather than with mercurous iodide. Except for ethyl-butyl sulfide, 2 mercuric iodide groups are taken up for each atom of sulfur present. A part of the iodine may enter the molecule by substitution and the other part remains in the mother liquor from which the compounds separate. In a number of instances these mother liquors were titrated for iodine and, in all cases, very nearly the calculated amount of iodine was found. They were found to be acid to litmus. The mother liquors from the 2 compounds with mercurous iodide mentioned above, contained no iodine.

To prepare these compounds, 2 to 5 g. mercuric iodide was suspended in 50 cc. of acetone, and the sulfide was added slowly while the mixture was shaken and cooled. The disappearance of red mercuric iodide determined the end of the reaction. This required about 2 mols of the sulfide to 1 mol of the mercuric iodide in the first 5 preparations and about 1:1 for the other 4. Sometimes white or yellow crystals appeared immediately, while in some cases the addition of alcohol was necessary to precipitate the compound.

The compounds which separated readily from acetone were recrystallized from it, the others, from alcohol.

The compounds and their analyses are given in Table III.

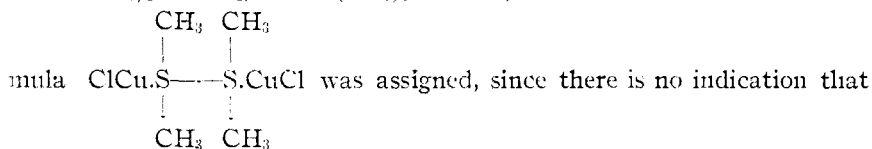
TABLE III.

Compound.	Color and form.	M. p. °C.	Hg calc. %.	Found. %.	I calc. %.	Found. %.
$2\text{C}_2\text{H}_5\text{SC}_4\text{H}_9 \cdot 3\text{HgI}_2$	white plates	163	49.38	49.14	32.06	32.33
$\text{C}_4\text{H}_9\text{SCH}_2\text{SC}_4\text{H}_9 \cdot \text{HgI}_2$	small cryst.	89	31.02	30.85	39.26	39.22
$\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{SC}_4\text{H}_9 \cdot \text{HgI}_2$	white plates	85	30.36	30.41
$\text{C}_2\text{H}_5\text{OCHISC}_4\text{H}_9 \cdot (\text{HgI})_2$	yellow plates	156	43.16	43.42	40.98	41.17
$\text{C}_6\text{H}_5\text{COCH}_2\text{SC}_4\text{H}_9 \cdot (\text{HgI})_2$	yellow plates	158	46.48	46.60	29.41	29.67
$\text{CH}_3\text{CI}(\text{SC}_4\text{H}_9)_2 \cdot (\text{HgI})_4$	yellow plates	138	48.86	48.83	38.65	38.44
$(\text{CH}_2\text{I})_2\text{C}(\text{SC}_4\text{H}_9)_2 \cdot (\text{HgI})_4$	yellow plates	159	45.30	45.50	42.97	42.68
$\text{C}_6\text{H}_5\text{CI}(\text{SC}_4\text{H}_9)_2 \cdot (\text{HgI})_4$	yellow plates	86	47.08	47.17	37.23	36.93
$\text{C}_6\text{H}_5(\text{CH}_2\text{I})\text{C}(\text{SC}_4\text{H}_9)_2 \cdot (\text{HgI})_4$	yellow plates	155	46.72	46.84	36.93	36.75

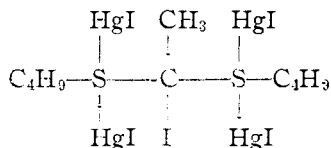
The sulfur in (1) was found to be 5.05, calc. 5.26%; and in (4) 3.45, calc. 3.33%.

Discussion.

Phillips¹ has observed that methyl sulfide and cupric chloride do not form $(\text{CH}_3)_2\text{S}\cdot\text{CuCl}_2$, but $2(\text{CH}_3)_2\text{S}\cdot 2\text{CuCl}$, to which the structural for-



mula was assigned, since there is no indication that the copper has been reduced. Similarly, auric chloride unites with the same sulfide to form $\text{ClAu}\cdot\text{S}(\text{CH}_3)_2$. We may assume, with Phillips, that the sulfur in our compounds has a valence of 4 and write:

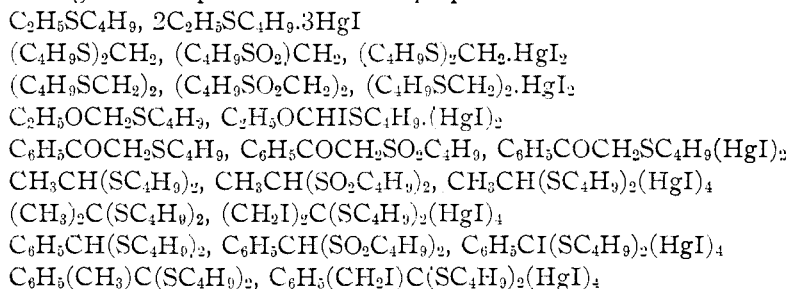


Tschugaeff² has obtained crystalline derivatives of the type $\text{CuCl} \text{---} \text{RSCH}_2\text{CH}_2\text{SR}$ which correspond with 2 of ours.

The only compound of a new type which we obtained is represented by the formula $2\text{C}_2\text{H}_5\text{SC}_4\text{H}_9\cdot 3\text{HgI}$, obtained from ethyl-butyl sulfide, which is similar to $2(\text{CH}_3)_2\text{S}\cdot 3\text{HgCl}_2$ obtained by Phillips, except that in this case we have mercuric iodide instead of mercurous iodide.

Summary.

A number of derivatives have been made from butyl mercaptan. The following new compounds have been prepared:



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¹ Phillips, *THIS JOURNAL*, **23**, 256 (1901).

² Tschugaeff, *Ber.*, **41**, 2226 (1908).