

Benzoic Acid, in the presence of salicylic, acetic, tartaric, citric, oxalic, and succinic acids.

Fumaric Acid, in the presence of maleic and succinic acids.

Cinnamic Acid, in the presence of benzoic acid.

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

A SULFIDE ALCOHOL, OR BUTYL MERCAPTO-ETHYL ALCOHOL.¹

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In a recent article from this laboratory,² the acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{COOH}$, was studied with respect to the influence of the sulfur atom on the chemical and physical properties. In the present investigation, the corresponding alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$, has been studied with the same object in view.

This alcohol is obtained readily by the action of ethylene chlorohydrine on the sodium salt of butyl mercaptan in water solution. It is a colorless oil boiling at $92\text{--}3^\circ$ at 3 mm. In its physical properties and in its reactions, it resembles one of the higher alcohols, though some differences are found. Its odor suggests a higher alcohol and a sulfide, though the odor of its acetate is much more like that of an acetate of a higher alcohol. The chloride and bromide are readily prepared from the alcohol by the usual methods, but it shows very slight tendency to combine with phthalic anhydride. The sulfur atom appears to exercise somewhat the same influence on the mobility of the groups in the β -position as in the sulfide acid and in mustard gas, though the influence is less evident here. The acetate of this alcohol is stable, while the diacetate corresponding to mustard gas is very unstable.

From the bromide, $\text{BuSCH}_2\text{CH}_2\text{Br}$, the sulfide, $\text{BuSCH}_2\text{CH}_2\text{SBu}$, was readily obtained, but the corresponding sulfide ether, $\text{BuSCH}_2\text{CH}_2\text{OEt}$, could not be prepared by heating the bromide with sodium ethylate, vinyl-butyl sulfide, $\text{BuSCH} : \text{CH}_2$, was formed instead. This substance added hydrobromic acid readily to give the original bromide instead of the secondary bromide, BuSCHBrCH_3 which we desired.

The properties of the alcohol and its derivatives are brought together in the following table.

TABLE I.

Compound.	B. p.	d_0^0	d_{25}^{25}	n_D^{20}
$\text{BuSCH}_2\text{CH}_2\text{OH}$	$92\text{--}3^\circ$ at 3 mm.	0.9828	0.9693	1.4800
$\text{BuSCH}_2\text{CH}_2\text{OCOCH}_3$	84° at 4 mm.	1.0043	0.9875	1.4648
$\text{BuSCH}_2\text{CH}_2\text{Cl}$	68° at 6 mm.	1.0315	1.0101	1.4825
$\text{BuSCH}_2\text{CH}_2\text{Br}$	74° at 3 mm.	1.2308	1.2089	1.6740

¹ This and the following article are from the Doctor's dissertation of Thomas Cobb Whitner, Jr.

² Uyeda and Reid, *THIS JOURNAL*, **42**, 2385 (1920).

Experimental.

The Alcohol, Butyl Mercapto-ethyl Alcohol.—To 40 g. of caustic soda and 90 g. of butyl mercaptan dissolved in 250 cc. of water, 80 g. of chlorohydrine was added. The mixture was boiled under a reflux condenser for one hour and distilled with steam to eliminate impurities. The alcohol remained behind; it was separated, dried, and distilled *in vacuo*. Yield, 108 g.

The Acetate, Butyl Mercapto-ethyl Acetate.—The alcohol was mixed with an equal amount of acetyl chloride and the mixture allowed to stand for some hours. The product was washed thoroughly with water, then dried over calcium chloride and distilled.

Analysis. Subs., 1.7100: 0.5441 g. KOH required for saponification. Calc.: 0.5448.

The Chloride, Butyl Mercapto-ethyl Chloride.—A mixture of 30 g. of the alcohol and 32 cc. of conc. hydrochloric acid was boiled under a reflux condenser for 4 hours, with the further addition of 10 cc. of the acid during this operation. The mixture was homogeneous at first, but soon separated into 2 layers. The chloride was washed thoroughly, dried, and distilled.

Analysis. Calc.: Cl, 23.25. Found: 22.96.

The Bromide, Butyl Mercapto-ethyl Bromide.—This compound was prepared in several slightly different ways. (1) A mixture of 30 g. of the alcohol and 72 g. (2 molecules) of constant-boiling hydrobromic acid was boiled for 8 hours; yield, 13 g. (2) Dry hydrogen bromide was passed for 3 hours into 50 g. of the alcohol which was kept cold; yield, 20 g., or 27%. (3) Dry hydrogen bromide was passed for 3 hours into a mixture of 50 g. of the alcohol and a little red phosphorus kept at a temperature of 30–40°; yield, 30 g., or 41%. (4) A mixture of 90 g. of the alcohol and 125 g. of constant-boiling hydrobromic acid (3.5 molecules) was boiled for 3 hours under a reflux condenser; yield, 68 g., or 51%. In all cases the layer of bromide was separated, washed carefully, and distilled.

Analysis. Calc.: Br, 40.57; S, 16.28. Found: Br, 40.40; S, 15.93.

Dibutyl Ethylene Sulfide, BuSCH₂CH₂SBu.—To a solution of 5 g. of sodium in 100 cc. of alcohol, 20 g. of butyl mercaptan and 40 g. of the bromide just described were added. The mixture was refluxed for a time, water was added, and the oily layer was separated, dried and fractioned. The main portion boiled at 130° at 5 mm. pressure and proved identical with a product, to be described later, which was obtained by the action of ethylene bromide upon butyl mercaptan.

Vinyl-butyl Sulfide.—To 75 cc. of alcohol in which 6 g. of sodium had been dissolved, 35 g. of the bromide was added and the mixture was heated for 30 minutes. Water was added and the oily layer washed and dried. Under atmospheric pressure, this began to distil at 150°, but the boiling point rose steadily to 217°. Helfrich and Reid¹ had a similar experience with vinyl sulfide. Several preparations were made, but no material of constant properties could be obtained. That vinyl-butyl sulfide was present seems to be shown by the following experiments. Bromine was absorbed rapidly by a chloroform solution but the desired dibromide could not be obtained; complicated reactions appear to take place. A chloroform solution of the product was saturated with hydrobromic acid. After the solution had stood during the night, it was saturated with hydrogen bromide again. When the chloroform was removed and the product had been fractioned in vacuum, an oil boiling at 75° under 4 mm. pressure was obtained, d_4^{25} 1.2253, and d_{25}^{25} 1.2075, and contained 40.38% of bromine instead of 40.57 as calculated for the monobromide. Since the density does not agree with that of the original primary bromide, it was hoped that it might be the secondary

¹ Helfrich and Reid, *THIS JOURNAL*, 42, 1225 (1920).

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*- $\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{Br}$, butyl mercapto-ethyl bromide.

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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.