and a mixed melting point of the two was 173–175°. The yield was 2.9 g. (36%).

Hydrogenation of Ethyl Acetoacetate.—Ten grams of ethyl acetoacetate, about 50 g. of Raney nickel catalyst and 150 ml. of ethyl alcohol were refluxed for five hours. The nickel was removed by centrifuging, the alcohol distilled, and the product distilled; b. p. 175–183°. The yield was 9.8 g. (96%). A sample of the product did not absorb any more hydrogen when subjected to hydrogenation under pressure, and did not form a 2,4-dinitrophenylhydrazone,[11] indicating that the ethyl acetoacetate was completely reduced to ethyl β-hydroxybutyrate. Saponification equivalent found was 133.7 (calcd. 132.2).

Hydrogenation of Benzalacetone.—Five grams of benzalacetone was refluxed with about 25 g. of Raney nickel catalyst and 100 ml. of ethyl alcohol for two hours, and the nickel removed by centrifuging. The alcohols were distilled and the product came over at 234°. The yield was 3.9 g. (75%).

The phenylurethan of the 4-phenyl-2-butanol, recrystallized from petroleum ether, melted at 114–115°. The melting point of this compound is given as 113°.[12]

Hydrogenation of Benzaldehyde.—Five grams of benzaldehyde, about 25 g. of Raney nickel catalyst and 100 ml. of alcohol were refluxed for two hours. The nickel was centrifuged from the solution and the product steam-distilled from the mixture. It measured 3.6 ml. (3.1 g., 78%) and was identified as toluene by its boiling point, 108–110°.

Hydrogenation of Acetone.—Five grams of acetone was refluxed with 25 g. of Raney nickel catalyst and 100 ml. of water for one and one-half hours. The nickel was centrifuged and the product distilled, along with some water. It was salted out with potassium carbonate; 4.9 cc. (4.0 g.; 78%).

The 3,5-dinitrobenzoate, recrystallized from ethyl alcohol, melted at 122–123°; the melting point of isopropyl 3,5-dinitrobenzoate is 123°.[13]

The product gave a negative test with 2,4-dinitrophenylhydrazine, indicating complete reduction.

Hydrogenation of Eugenol.—A solution of 2 g. of eugenol in 135 ml. of 70% ethyl alcohol was refluxed for five hours with about 25 g. of Raney nickel catalyst. The nickel and alcohol were removed. Benzene was added and removed by distillation in order to remove traces of ethyl alcohol. The residue gave 2.9 g. (75%) of dihydroeugenol *p*-nitrobenzoate, m. p. 73–74° (after crystallization from methanol).

Anal. Calcd. for $C_{17}H_{17}O_5N$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.78; H, 5.61; N, 4.59.

Hydrogenation of Cholesterol.—Three runs were made, using 2 g. of cholesterol, about 25 g. of Raney nickel catalyst and 100 ml. of ethyl alcohol, and refluxing for five hours. The nickel was removed, and the solution concentrated. Crystals came out on cooling the solution and were collected and dried. In the first two runs, the product melted at 123–129°; in the third run, at 117–121°. Recrystallization from ethyl alcohol did not change these melting points, and their long range indicates the presence of more than one compound. Because of the possibility of incomplete reduction, the crystals from the third run were refluxed in 100 ml. of alcohol with 15 g. of fresh Raney nickel catalyst for three hours. The crystals obtained melted at 117–121°. Since the product gave a positive test for unsaturation,[14] the reduction was not complete.

Acknowledgment.—The authors wish to express their appreciation to Mrs. E. H. Meiss and Messrs. R. N. Boos and H. S. Clark for carrying out the microanalyses.

Summary

1. Under the conditions used for the hydrogenolysis of sulfides, carbon to carbon double bonds, carbonyls, nitro groups, hydrazo and azoxy linkages are reduced. Likewise, benzyl alcohol gives toluene.

2. Benzene rings, acids and esters are stable to reduction by this procedure.

3. Alkylation of an amine by ethyl alcohol in the presence of Raney nickel catalyst at 78° has been observed.

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[11] Brady, *J. Chem. Soc.*, 756 (1931).

[12] Klages, *Ber.*, **37**, 2313 (1904).

[13] Bryant, THIS JOURNAL, **54**, 3758 (1932); Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

[14] Liebermann, *Ber.*, **18**, 1803 (1885); Burchard, Inaugural Dissertation, Rostock, 1889; cf. *Chem. Zentr.*, **61**, 25 (1890).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Novel Product from the Alkaline Hydrolysis of a Quaternary Ammonium Bunte Salt[1]

BY H. R. SNYDER AND G. RICHARD HANDRICK[2]

Benzyldimethylphenylammonium S-benzylthiosulfate, first encountered as a product of the reaction of benzyldimethylphenylammonium chloride and sodium thiosulfate,[3] decomposes on mild treatment with aqueous alkali to form dimethylaniline, benzoic acid, benzyl sulfide and benzyl disulfide. Evidently part of the reactions which occur are similar to those observed earlier[4] in the alkaline hydrolysis of the metal salts of alkyl- and arylthiosulfates. Thus, sodium S-benzylthiosulfate[4a] gave benzoic acid, thiobenzoic acid and benzyl disulfide. In order to characterize other products of the present reaction, and in particular to learn the fate of the benzyl group in the cation of the salt, benzyldimethylphenylammonium S-*p*-bromobenzylthiosulfate has been subjected to the action of aqueous alkali. The various products which have been identified are shown in the equation.

$$[p\text{-BrC}_6\text{H}_4\text{CH}_2\text{SSO}_3]^- \ [\text{C}_6\text{H}_5\text{CH}_2\text{N(CH}_3)_2\text{C}_6\text{H}_5]^+ \xrightarrow{\text{KOH}}$$
$$\text{C}_6\text{H}_5\text{N(CH}_3)_2 + p\text{-BrC}_6\text{H}_4\text{CHO} + p\text{-BrC}_6\text{H}_4\text{CO}_2\text{K} +$$
$$(p\text{-BrC}_6\text{H}_4\text{C}_2\text{H}_2\text{S})_2 + \text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_4\text{Br}(p) +$$
$$\text{C}_{14}\text{H}_{12}\text{S}_2\text{O}_2\text{BrK}$$

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[1] This is the fifth communication on reactions of quaternary ammonium salts; for the fourth, see THIS JOURNAL, **66**, 350 (1944).

[2] Present address: the University of Pennsylvania, Philadelphia, Pa.

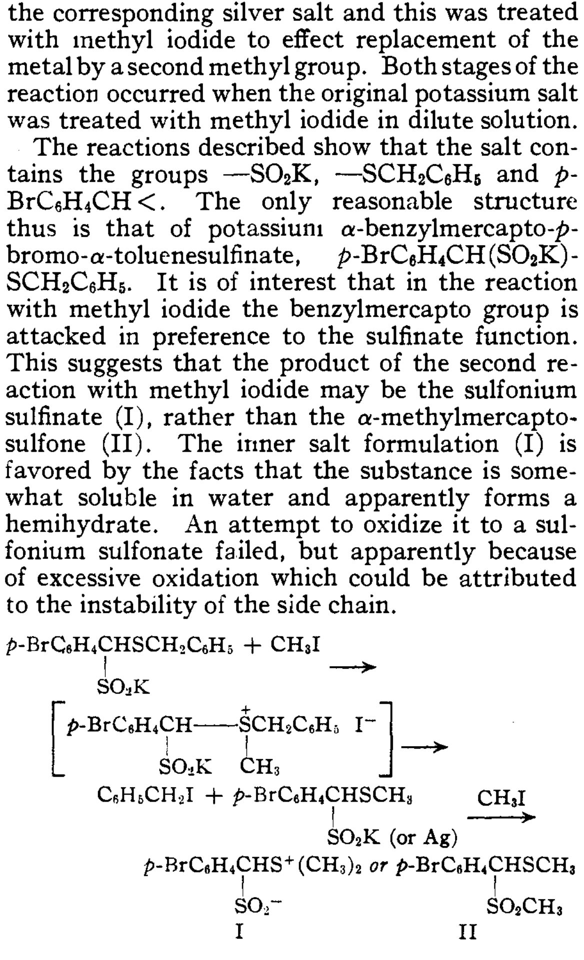
[3] Snyder and Speck, THIS JOURNAL, **61**, 668 (1939).

[4] (a) Price and Twiss, *J. Chem. Soc.*, **93**, 1395 (1908); **97**, 1175 (1910); (b) Baumgarten, *Ber.*, **63**, 1330 (1930).

The reaction leading to *p*-bromobenzaldehyde, *p*-bromobenzoic acid and benzyl *p*-bromobenzyl sulfide may be related to that of benzyl disulfide with benzyl chloride and alkali,[4a] which yields, among other products, benzyl sulfide, benzaldehyde and benzoic acid. In the present instance the benzyldimethylphenylammonium ion may be assuming the role of the benzyl chloride.

The most interesting of the products obtained in the present work was the salt, $C_{14}H_{12}S_2O_2BrK$. Preparation of analytical samples of the potassium salt, the free acid and other of its salts proved extremely difficult because of the thermal instability and strongly hygroscopic character of the compounds. The free acid decomposed rapidly at 150° to yield *p*-bromobenzaldehyde and its benzyl mercaptal. The potassium salt was evidently a sulfinate, for it was attacked by hydrogen peroxide or dilute potassium permanganate to produce a new salt containing one more atom of oxygen. When the original potassium salt was treated with methyl iodide a new salt, $C_8H_8S_2O_2BrK$, was obtained; comparison of this formula with that of the original salt indicates the replacement of a benzyl group by a methyl group. The other product of the reaction, indeed, was benzyl iodide. The new salt was converted to the corresponding silver salt and this was treated with methyl iodide to effect replacement of the metal by a second methyl group. Both stages of the reaction occurred when the original potassium salt was treated with methyl iodide in dilute solution.

The reactions described show that the salt contains the groups $—SO_2K$, $—SCH_2C_6H_5$ and $p\text{-}BrC_6H_4CH<$. The only reasonable structure thus is that of potassium α-benzylmercapto-*p*-bromo-α-toluenesulfinate, $p\text{-}BrC_6H_4CH(SO_2K)\text{-}SCH_2C_6H_5$. It is of interest that in the reaction with methyl iodide the benzylmercapto group is attacked in preference to the sulfinate function. This suggests that the product of the second reaction with methyl iodide may be the sulfonium sulfinate (I), rather than the α-methylmercaptosulfone (II). The inner salt formulation (I) is favored by the facts that the substance is somewhat soluble in water and apparently forms a hemihydrate. An attempt to oxidize it to a sulfonium sulfonate failed, but apparently because of excessive oxidation which could be attributed to the instability of the side chain.



$$\underset{\displaystyle SO_2K}{p\text{-}BrC_6H_4CH}SCH_2C_6H_5 + CH_3I \longrightarrow$$

$$\left[\underset{\displaystyle SO_2K}{p\text{-}BrC_6H_4CH}—\underset{\displaystyle CH_3}{\overset{+}{S}}CH_2C_6H_5\ I^-\right] \longrightarrow$$

$$C_6H_5CH_2I + \underset{\displaystyle SO_2K\ (or\ Ag)}{p\text{-}BrC_6H_4CH}SCH_3 \xrightarrow{CH_3I}$$

$$\underset{\displaystyle \underset{\displaystyle I}{SO_2^-}}{p\text{-}BrC_6H_4CH}S^+(CH_3)_2 \text{ or } \underset{\displaystyle \underset{\displaystyle II}{SO_2CH_3}}{p\text{-}BrC_6H_4CH}SCH_3$$

The mode of formation of α-benzylmercapto-*p*-bromo-α-toluenesulfinate is still obscure. Evidently the benzylmercapto group in this salt, as well as that in benzyl *p*-bromobenzyl sulfide, is generated through benzylation by the benzyldimethylphenylammonium ion. Reactions of oxidation and reduction and of rearrangement or substitution also must be concerned in the formation of the salt.

Experimental

Benzyldimethylphenylammonium S-*p*-Bromobenzylthiosulfate.—A solution of sodium S-*p*-bromobenzylthiosulfate was prepared by refluxing a mixture of 474 g. of *p*-bromobenzyl bromide, 500 ml. of ethanol, 470 g. of sodium thiosulfate pentahydrate and 800 ml. of water. When the hot mixture became homogeneous it was cooled and added to 470 g. of benzyldimethylphenylammonium chloride dissolved in 500 ml. of water. The yield of the quaternary thiosulfate was 666 g. or 71%; m. p. 124–125°.

Anal. Calcd. for $C_{22}H_{24}O_3NS_2Br$: Br, 16.17. Found: Br, 16.09.

Decomposition of the Quaternary Ammonium S-Alkylthiosulfates.—The procedure employed for the decomposition with aqueous alkali consisted in passing steam through a mixture of the quaternary ammonium salt with a 10% solution of the reagent. A red oil formed immediately and the tertiary amine steam distilled. The distillation was continued until small droplets of the red oil began to appear in the condenser. In general the reaction was complete within two hours.

The distillate was extracted with ether and the water layer discarded. The basic and acidic products were removed from the ether extract by washing with dilute hydrochloric acid and with aqueous sodium carbonate. The ether solution was evaporated and any residual neutral material was steam distilled again to separate any of the less volatile red oil which may have been carried over in the original steam distillation.

The residue from the original steam distillation was made strongly alkaline and allowed to stand overnight. It was then shaken with ether and filtered to separate any precipitated solid from the liquid layers. The solid was washed with ether until colorless and purified further by crystallization. The layers in the filtrate were separated. The ether layer was washed with water, then with dilute hydrochloric acid. The acid washing was combined with the similar washings from the treatment of the steam distillate. The ether layer was washed again with water and dried over anhydrous magnesium sulfate. The solvent was removed on a steam-bath from the non-volatile neutral product.

The water layer from the filtration was extracted with chloroform to separate an ether insoluble oil. It was then made acid with concentrated hydrochloric acid, cooled, and filtered. The filtrate was discarded and the solid acidic product was recrystallized.

Unless stated otherwise the solid products were identified by mixed melting points with authentic samples. The yields given are based on one mole of product from one mole of quaternary salt.

Cleavage of Benzyldimethylphenylammonium S-Benzylthiosulfate.—The decomposition of 29.4 g. of benzyldimethylphenylammonium S-benzylthiosulfate by 200 ml. of 10% sodium hydroxide was carried out and the products were separated as described above. The cleavage was apparently complete within thirty minutes.

Dimethylaniline, identified by physical constants, was the only organic material found in the distillate. The amount recovered was 4.8 g. or 59.2%.

Benzoic acid was isolated from the residue. The yield was 0.7 g. (8%).

The red oil which was separated from the residue as the neutral fraction decomposed upon distillation. The brown solid which remained when a portion of the oil was distilled at atmospheric pressure was recrystallized from alcohol and identified as benzyl sulfone, m. p. 146–148°. Distillation of the red oil under diminished pressure gave a pink solid, b. p. 136–145° (2 mm.). After recrystallization from 70% alcohol this was identified as benzyl sulfide, m. p. 47–48°.

In another experiment 10.6 g. of benzyldimethylphenylammonium S-benzylthiosulfate was heated for two hours on a steam-bath with 4.2 g. of potassium hydroxide in 100 ml. of water. At the end of this time the mixture was steam distilled and separated as before. From the red oil recovered, pink crystals of benzyl disulfide (m. p. 68–70°) separated.

Cleavage of Benzyldimethylphenylammonium S-*p*-Bromobenzylthiosulfate.—(a) By aqueous potassium hydroxide.—In a 500-ml. round-bottomed flask 49.4 g. of the quaternary thiosulfate was subjected to steam distillation in the presence of 100 ml. of a 10% solution of potassium hydroxide as described above. The following compounds were identified (the yields given are those obtained from several decompositions):

Dimethylaniline was recovered from the distillate in 70 to 82% yield of the theoretical amount.

p-Bromobenzaldehyde (m. p. 59–60°) was recovered from the distillate in 1 to 4% yield. The semicarbazone (m. p. 231–232°; lit.,[5] 227–228°) and the 2,4-dinitrophenylhydrazone (m. p. 260–261°) were prepared. The latter derivative apparently is new and was analyzed.

Anal. Calcd. for $C_{13}H_9O_4N_4Br$: N, 15.34. Found: N, 15.51.

Benzyl *p*-bromobenzyl sulfide and *p*-bromobenzyl disulfide were the constituents of the neutral red oil. After standing at room temperature for four weeks with low boiling petroleum ether, the oil deposited a solid which was collected and washed with petroleum ether until white: m. p. 86–89°. A mixed melting point with an authentic sample showed this to be *p*-bromobenzyl disulfide (m. p. 88–89°).[6] The petroleum ether was evaporated from the filtrate. The residual red liquid was dissolved in glacial acetic acid and oxidized by an excess of hydrogen peroxide. The white solid which separated when the mixture was cooled was recrystallized from ethanol and shown to be benzyl *p*-bromobenzyl sulfone, m. p. 174–176°. A small quantity of the original red oil also was oxidized in glacial acetic acid by an excess of hydrogen peroxide. The only insoluble products which could be isolated were benzyl *p*-bromobenzyl sulfone and *p*-bromobenzoic acid. Authentic benzyl *p*-bromobenzyl sulfone for the mixed melting point was prepared by oxidizing crude benzyl *p*-bromobenzyl sulfide. The sulfide was prepared from potassium benzylmercaptide and *p*-bromobenzyl bromide; it was an orange oil which decomposed during attempted distillation at 2 mm. The crude sulfide was dissolved in glacial acetic acid and refluxed with a two-fold excess of 30% hydrogen peroxide until the color changed from red to pale yellow. The reaction mixture was poured into ice water. Benzyl ***p*-bromobenzyl sulfone** was recrystallized from ethanol; m. p., 174–176°.

Anal. Calcd. for $C_{14}H_{13}O_2SBr$: S, 9.84; Br, 24.60. Found: S, 9.63; Br, 24.83.

Benzyl *p*-bromobenzyl sulfoxide was obtained when a mixture of 0.83 g. of the crude sulfide, 1.5 ml. of 30% hydrogen peroxide and 20 ml. of ethanol was refluxed for five hours. After recrystallization from high-boiling petroleum ether it melted at 139–139.5°.

Anal. Calcd. for $C_{14}H_{13}OSBr$: Br, 25.90: Found: Br, 26.00.

The organic salt from the residue of the steam distillation, shown in later experiments to be potassium α-benzylmercapto-*p*-bromo-α-toluenesulfinate, melted at 220–221°. The yield was 7 to 16%.

Anal. Calcd. for $C_{14}H_{12}O_2S_2BrK \cdot 3/2H_2O$: C, 39.80; H, 3.56; S, 15.20; Br, 19.00; K, 9.25. Found: C, 41.17; H, 3.69; S, 14.60; Br, 18.54; K. 8.95.

p-Bromobenzoic acid (m. p. 255–256°) constituted the acid fraction of the residue from the steam distillation. The yield was 5 to 12%.

(b) **By Alcoholic Potassium Hydroxide.**—To 9.8 g. of the quaternary salt was added a filtered solution of 5.6 g. of potassium hydroxide in 100 ml. of hot 95% ethanol. The reaction mixture was refluxed for forty-five minutes. The precipitate which formed was separated by filtration and proved to be potassium sulfite (3 g., 97%). The filtrate was evaporated to 50 ml. and added to 250 ml. of 10% potassium hydroxide. This solution was extracted three times with ether. Acidification of the alkaline water solution yielded 0.5 g. of *p*-bromobenzoic acid (12.5%). The ether layer was washed once with water, and then thoroughly extracted with dilute hydrochloric acid. Dimethyl-aniline (1.5 g., 66.4%) was recovered from neutralization of the hydrochloric acid solution by sodium carbonate. The ether solution was washed again with water, dried over anhydrous magnesium sulfate, and evaporated. The residue consisted of 4.8 g. of a red oil. A portion was oxidized in acetic acid by excess hydrogen peroxide (30%) to produce benzyl *p*-bromobenzyl sulfone.

Derivatives of α-Benzylmercapto-*p*-bromo-α-toluenesulfinic acid: (a) **The *p*-bromobenzylisothiouronium salt,** prepared from the potassium salt in water and *p*-bromobenzylisothiouronium bromide[7] in alcohol, was recrystallized from alcohol; m. p. 209–211°.

Anal. Calcd. for $C_{22}H_{22}O_2N_2S_3Br_2 \cdot H_2O$: C, 42.60; H, 3.88; N, 4.51; S, 15.50; Br, 25.80. Found: C, 43.28; H, 4.15; N, 4.72; S, 14.76; Br, 25.59.

(b) **The magnesium salt,** prepared by adding an equivalent amount of a water solution of magnesium chloride to a warm aqueous solution of potassium α-benzylmercapto-*p*-bromo-α-toluenesulfinate, recrystallized from water in shining plates; m. p. 219–220°. After dehydration in an Abderhalden drying pistol for twenty hours at 65°, this compound had turned pink, and melted at 197–198°.

Anal. Calcd. for $C_{28}H_{24}O_4S_4Br_2Mg \cdot 5H_2O$: C, 41.00; H, 4.15; S, 14.90; Br, 19.50; Mg, 2.96. Found: C, 40.57; H, 4.12; S, 14.77; Br, 20.00; Mg, 2.82.

(c) **The silver salt** was prepared from an excess of a 5% solution of silver nitrate and an aqueous solution of potassium α-benzylmercapto-*p*-bromo-α-toluenesulfinate. The precipitate which formed was recrystallized from absolute ethanol; m. p. 149–150° (dec.).

Anal. Calcd. for $C_{14}H_{12}O_2S_2BrAg \cdot 3/2H_2O$: Ag, 22.5. Found: Ag, 21.7.

(d) **The free acid** was prepared from 1 g. of the potassium salt in 7 ml, of water and 10 ml. of concentrated hydrochloric acid. Cooling caused the resulting oil to crystallize. The solid was collected, washed with 1:1 hydrochloric acid, and dried in a desiccator over potassium hydroxide. The yield was 0.8 g. or 83%. Although this acid decomposes upon prolonged refluxing with the solvent, it can be recrystallized from benzene; m. p., 109–110° (dec.).

Anal. Calcd. for $C_{14}H_{13}O_2S_2Br \cdot 3/2H_2O$: C, 43.80; H, 4.17; S, 16.66; Br, 20.82. Found: C, 42.50; H, 4.11; S. 15.35; Br, 20.45.

Reactions of α-Benzylmercapto-*p*-bromo-α-toluenesulfinic Acid and its Derivatives

(a) **Pyrolysis.**—One gram of the acid was decomposed in a flask fitted with an air condenser by heating for ten minutes in an oil-bath maintained at 150–160°. The residue was dissolved in ether and filtered from a small amount of a gray precipitate. The ether solution was concentrated on a steam-bath, and the liquid remaining was steam distilled. The white solid which collected in the distillate was filtered, washed with dilute potassium hydroxide and recrystallized from 60% ethanol. It proved to be *p*-bromobenzaldehyde (m. p. 59–60°). The residue from this steam distillation was dissolved in ether, washed with dilute sodium carbonate, water, dilute hydrochloric acid, again with water, and dried over anhydrous magnesium sulfate.

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(5) Van der Lee, *Rec. trav. chim.*, **45**, 279 (1926).

(6) Jackson and Hartshorn, *Am. Chem. J.*, **5**, 269 (1883).

(7) Dewey and Shaskey, THIS JOURNAL, **63**, 3526 (1941).

The amber oil which remained after the ether had been removed slowly crystallized in star-shaped clusters; m. p. 61–63°. This melting point was not depressed by admixture of authentic *p*-bromobenzaldehyde benzylmercaptal.

Anal. Calcd. for $C_{21}H_{19}S_2Br$: C, 60.72; H, 4.58. Found: C, 61.36; H, 4.88.

The sample for the mixed melting point was prepared from *p*-bromobenzaldehyde and benzylmercaptan by a method used for benzaldehyde benzylmercaptal.[8] This sample melted at 64–65°.

(b) **Oxidation.**—A solution of 2.2 g. of the potassium salt in 25 ml. of glacial acetic acid was heated under reflux with 20-ml. of 30% hydrogen peroxide for one hour. The solid obtained by evaporation of the solution over potassium hydroxide was washed with ether and acetone and crystallized from water. It was recrystallized from a mixture of equal volumes of absolute ethanol and benzene; m. p. 251–253°. The *p*-bromobenzylisothiouronium salt, m. p., 203–205° after recrystallization from 50% ethanol, was analyzed.

Anal. Calcd. for $C_{22}H_{22}O_3N_2S_3Br_2 \cdot H_2O$: C, 41.50; H, 3.77; N, 4.40. Found: C, 41.28; H, 3.69; N, 4.57.

The same salt was obtained more conveniently by oxidation in aqueous solution with an excess of potassium permanganate in the presence of a trace of acetic acid, decolorization with sodium sulfite, neutralization with sodium carbonate and precipitation with *p*-bromobenzylisothiouronium bromide.

(c) **Reactions with Methyl Iodide.**—A solution of 5.0 g. of potassium α-benzylmercapto-*p*-bromo-α-toluenesulfinate, 18 ml. (41 g.) of methyl iodide, and 250 ml. of acetone was refluxed for four days. At the end of this time a large amount of precipitate had formed and the solution was red in color. The mixture was cooled and filtered and the precipitate was washed with ether until it was colorless. It was caused to crystallize from absolute alcohol by the addition of an equal volume of benzene; m. p. 218–219°. The yield of **potassium α-methylmercapto-*p*-bromo-α-toluenesulfinate** was 3.0 g. or 75% of the theoretical amount.

Anal. Calcd. for $C_8H_8O_2S_2BrK \cdot 3/2H_2O$: C, 27.80; H, 3.18; Br, 23.10; K, 11.28. Found: C, 28.20; H, 3.08; Br, 22.62; K, 10.69.

The *p*-bromobenzylisothiouronium derivative was prepared and recrystallized three times from ethanol; m. p. 218–220°.

Anal. Calcd. for $C_{16}H_{18}O_2N_2S_3Br_2 \cdot H_2O$: C, 35.32; H, 3.68; N, 5.15; Br, 29.41. Found: C, 35.72; H, 3.85; N, 5.48; Br, 29.01.

The acetone mother liquors from the preparation of potassium α-methylmercapto-*p*-bromo-α-toluenesulfinate were concentrated on a steam-bath. The residue was taken up in ether. The solution was filtered from inorganic salts, and the ether was evaporated. Cooling in an ice–salt mixture caused crystals to form. These needles were separated by filtration through a cold funnel and recrystallized twice from 95% ethanol. The product, an extremely lachrymatory liquid at room temperature, was dried in a desiccator over potassium hydroxide and calcium chloride. Benzyl iodide melts at 24°.[9]

To the benzyl iodide dissolved in acetone was added 0.5 g. of mercuric iodide and 0.3 g. of benzyl sulfide. Two volumes of ether were added and the solution was allowed to stand. Overnight needles began to precipitate. More mercuric iodide was added until the solution was saturated and the color of the solution was light yellow. After standing another day the precipitate was collected on a filter and recrystallized from acetone–ether. The pale green needles (m. p. 139–140°) were shown by mixed melting point (140–141°) to be tribenzylsulfonium mercuric triiodide (m. p. 140–141°), an authentic sample of which was prepared by the procedure of Haas and Dougherty.[10]

The methylation product (I or II) was prepared by two methods.

An excess of a 5% solution of silver nitrate was added to an aqueous solution of potassium α-methylmercapto-*p*-bromo-α-toluenesulfinate. The precipitated silver salt was separated, dissolved in alcohol, and shaken with an excess of methyl iodide. The silver iodide which formed was separated by filtration and the filtrate was concentrated. An equal volume of ether was added to precipitate the product (I or II). After recrystallization from 95% ethanol it melted at 203° (dec.).

Anal. Calcd. for $C_9H_{11}O_2S_2Br \cdot 1/2H_2O$: C, 35.6; H, 3.95; S, 21.05. Found: C, 35.90; H, 4.02; S, 20.52.

The same compound was prepared by allowing a solution of 1.5 g. of potassium α-benzylmercapto-*p*-bromo-α-toluenesulfinate and 6 ml. (13.7 g.) of methyl iodide in 60 ml. of acetone to stand for two weeks at room temperature.

An attempt was made to oxidize this substance. One hundred milligrams of the product of methylation in the previous experiment was dissolved in 2 ml. of water and 1.4 ml. of acetic acid. To the solution heated at 70° on a water-bath dilute potassium permanganate solution was added until the purple color was permanent for thirty minutes. After decolorization with sodium bisulfite, the reaction mixture was cooled and the solid collected by filtration. Forty milligrams of the unchanged material (I or II) was recovered.

Summary

The alkaline hydrolysis of the benzyldimethylphenylammonium salts of S-benzyl- and S-*p*-bromobenzylthiosulfuric acids has been studied. In their main features, the reactions are similar to those which occur in the alkaline hydrolysis of the metal salts (Bunte salts), but sulfur-alkylation by the quaternary ammonium ion occurs also. One of the products from benzyldimethylphenylammonium S-*p*-bromobenzylthiosulfate has been shown to be the alkali salt of α-benzylmercapto-*p*-bromo-α-toluenesulfinic acid, *p*-BrC_6H_4-$CH(SO_2H)SCH_2C_6H_5$.

URBANA, ILLINOIS RECEIVED JULY 5, 1944

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[8] Fromm and Junius, *Ber.*, **28**, 1111 (1895).

[9] Kumpf, *Ann.*, **224**, 126 (1884).

[10] Haas and Dougherty, THIS JOURNAL, **62**, 1004 (1940).