[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI]

SULFONIUM COMPOUNDS. III. THE REACTION OF ORGANIC SULFIDES WITH ORGANIC SULFATES[1]

FRANCIS EARL RAY AND JOSSELYN LISZNIEWSKA FARMER[2]

Received May 24, 1943

In a previous paper of this series (1), Ray and Levine proposed a new mechanism for the sulfonium reaction which offered a satisfactory explanation for the formation of trimethylsulfonium iodide when higher alkyl sulfides react with methyl iodide. The mechanism postulates the formation of the normally expected sulfonium compound as an intermediate. This may dissociate in one, two, or three ways, depending on the complexity of the salt, to give halides and sulfides, which in turn can combine to form the same or different sulfonium halides. Subsequent research (2, 3) has served to confirm this theory.

While there were numerous cases substantiating this mechanism in the literature, there is no report, so far as we are aware, of the formation of any but the expected product when organic sulfides are treated with methyl sulfate.

$$\text{I}\quad R_2S + (CH_3)_2SO_4 \rightarrow R_2CH_3S{\cdot}CH_3SO_4 \xrightarrow{H_2O} R_2CH_3SHSO_4 + CH_3OH$$

If rearrangement can occur in the case of the sulfonium sulfates it is certainly not easily observed. This might be due to either or both of two factors. (a) The reaction of organic sulfides with methyl or ethyl sulfate occurs so readily that long continued heating is unnecessary. (b) The methylsulfonium sulfate is so soluble and hygroscopic that it might well have escaped detection. In fact this latter compound has always been converted to some derivative for identification purposes (4).

Kehrmann and Duttenhöfer (5) in 1905 discovered that aromatic sulfides react with dimethyl sulfate to give sulfonium compounds. They did not isolate the sulfates, however. This almost universal tendency not to isolate the sulfates as such, led Rây and Rây (6) in 1927 to state that "sulfonium sulfates have not as yet been isolated." Although this was true of the aliphatic sulfonium sulfates with which they were working, Fichter and Sjöstedt (7) as early as 1910 had unmistakably isolated tribenzylsulfonium sulfate.

Even earlier Zincke and Glahn (8) had claimed the preparation of 2,6-dinitrophenol-4-dimethylsulfonium sulfate but gave no melting point or analytical data. In 1908 Smiles and Hilditch (9) reported the isolation of S-phenetyl-3,3′-dinitrophenazothionium sulfate and described it as bright green when dried in a vacuum and dark blue when dried at 100°. Kehrmann, Lievermann, and Frumkine (10), however, contended that Smiles' compound was impure, and that their preparation of it yielded light straw-yellow prisms. Neither of these

---

[1] Abstract of a thesis presented to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the Ph.D. degree, June 1943.

[2] Laws Fellow in Chemistry 1942–43.

papers reported analyses of the sulfonium sulfate, but it was converted to other derivatives.

Richter (11) claimed the preparation of a triaryl-ortho-sulfurous acid but Libermann (12) showed that this was really *o,o′,o″*-trihydroxytritolylsulfonium sulfate.

The neutral salts are less usual than the bisulfates. By treating the sulfonium chloride in acetic acid solution with the equivalent amount of dilute sulfuric acid, the neutral salt, bis-*p,p′,p″*-trihydroxytriphenylsulfonium sulfate was obtained (13).

In their search for a suitable reagent for the identification of alkyl sulfides, Bost and Schultze (3) prepared a series of stable sulfonium sulfates from dialkyl-*p*-phenylphenacylsulfonium bromides with silver sulfate. All were bisulfates except that prepared from dimethyl sulfide.

Recently a number of patents have been issued for sulfonium sulfates. It is claimed that these are useful as wetting, foaming, and emulsifying agents; cleaning, dispersing, and stripping agents; disinfectants and fungicides (14).

The reaction between an organic sulfide and methyl sulfate gives first the methyl sulfate salt of the sulfonium compound (equation I). This on hydrolysis yields the sulfonium bisulfate and methyl alcohol.

The earliest isolation of a sulfonium methyl sulfate was accomplished by Auwers and Arndt (15). They treated *p*-thiocresol with dimethyl sulfate and obtained dimethyl-*p*-cresylsulfonium methyl sulfate. It was a solid melting at 97° and reportedly stable in water. The methyl sulfate obtained from the interaction of *p*-tolylethyl sulfide and dimethyl sulfate was an oil. Here is found the only indication in the literature of a rearrangement, for the oil, when subjected to distillation, gave *p*-tolyl*methyl* sulfide. Brand and Stallmann (16) observed that *o*-nitrophenyldimethylsulfonium methyl sulfate yellowed on long standing and supposed that *o*-nitrophenylmethyl sulfide was formed. It is possible that the volatile dimethyl sulfide was produced instead.

In none of these preparations, however, has any evidence been found for the rearranged sulfonium salts that are so commonly obtained in the synthesis of sulfonium halides. We felt, nevertheless, that a more careful search might enable us to isolate such rearranged products.

As the final product in the halide equilibrium is the trimethylsulfonium ion, we thought it likely that this ion might also be obtained in any sulfate rearrangement. But as previously remarked, trimethylsulfonium sulfate is too soluble and hygroscopic to be isolated. We sought, therefore, some derivative that could easily be analyzed and identified. The picrates used by Ray and Szasz (17) in an investigation of sulfonium salts of nitric and organic acids proved unsuitable as they could not be isolated in acid solution.

In 1917, Vanino and Mussgnug (18) prepared a double salt of trimethylsulfonium iodide with bismuth chloride which had a definite melting point. In the hope of obtaining a similar sulfate we treated a solution of trimethylsulfonium sulfate with an equivalent of bismuth chloride and obtained a crystalline compound melting at 245°. It was shown by analysis for carbon, hydrogen, bismuth, sulfur, and chlorine to consist of three molecules of trimethylsulfonium chloride to two molecules of bismuth chloride, $3(CH_3)_3SCl \cdot 2BiCl_3$. When an excess of bismuth chloride was used, a compound melting at 121° was obtained in which trimethylsulfonium chloride and bismuth chloride were combined in a 1:1 ratio, $(CH_3)_3SCl \cdot BiCl_3$.

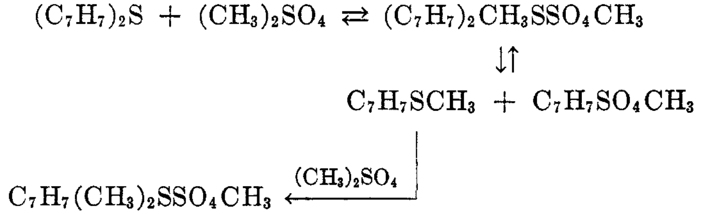
Blattler (19) claimed to have obtained a compound by treating trimethylsulfonium chloride with bismuth chloride. She gave no melting point and her analytical data were so inconclusive that she could not assign a formula to the product, which was probably contaminated with bismuth oxychloride. We repeated the preparation from trimethylsulfonium chloride and bismuth chloride and obtained the identical compounds, previously described.

No other bismuth chloride salts have been reported but Jörgensen (20) has described $3(C_2H_5)_3SBr \cdot 2BiBr_3$ but gave no analytical details. Kraut (21) reported that triethylsulfonium iodide combined in several ratios with bismuth iodide, but he gave no melting points for any of them. We obtained $(C_2H_5)_3SI \cdot BiI_3$ and found it to melt with decomposition at 218°. The early work on these double salts must, therefore, be considered unreliable as the possibility of contamination by bismuth oxyhalide was not guarded against.

In the present work it was decided to study the reaction between benzyl sulfide and dimethyl sulfate. Benzyl sulfide was selected because the high molecular weight of the benzyl radical should make its identification easy. In addition the well-known reactivity of the benzyl radical should favor rearrangement.

Benzyl sulfide and dimethyl sulfate in equimolar ratio in benzene solution were refluxed on the water-bath for thirty-six hours. Water was added and heating was continued until hydrolysis occurred. The aqueous layer was treated with bismuth chloride and a precipitate was obtained which on purification was found to be, not the normal dibenzylmethyl compound, but a benzyldimethyl derivative, $3(CH_3)_2C_7H_7SCl \cdot 2BiCl_3$. This may be expressed by the following series of reactions.

II



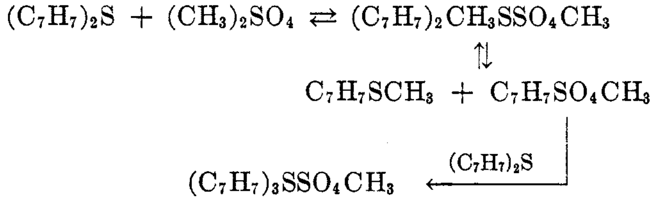
$$\begin{array}{l} (C_7H_7)_2S + (CH_3)_2SO_4 \rightleftarrows (C_7H_7)_2CH_3SSO_4CH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow\uparrow \\ \qquad\qquad\qquad\qquad C_7H_7SCH_3 + C_7H_7SO_4CH_3 \\ C_7H_7(CH_3)_2SSO_4CH_3 \xleftarrow{(CH_3)_2SO_4} \end{array}$$

This then is the first case of a rearrangement to be reported in the preparation of a sulfonium sulfate.

In this experiment, however, either the reaction did not reach equilibrium or the trimethylsulfonium compound is not of predominant stability as it is in the sulfonium halide equilibrium. If the first assumption is correct, then a higher temperature should hasten the establishment of equilibrium with the concommitant formation of trimethylsulfonium sulfate. In the second, an excess of benzyl sulfide should displace the reaction in the direction of the normal product, dibenzylmethylsulfonium sulfate.

We, therefore, heated *two* moles of benzyl sulfide with *one* mole of dimethyl sulfate in glacial acetic acid. The main product of this reaction was tribenzylsulfonium sulfate. Here, indeed, the reaction had been displaced in the direction anticipated, but it was displaced further than had been expected.

III



$$\begin{tikzcd}
(C_7H_7)_2S + (CH_3)_2SO_4 \arrow[r, leftrightarrow] & (C_7H_7)_2CH_3SSO_4CH_3 \arrow[d, leftrightarrow] \\
(C_7H_7)_3SSO_4CH_3 & C_7H_7SCH_3 + C_7H_7SO_4CH_3 \arrow[l, "(C_7H_7)_2S"']
\end{tikzcd}$$

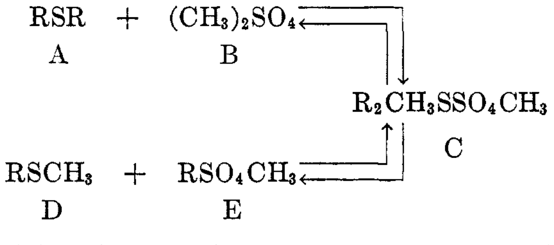
Sulfonium sulfates have also been prepared by the reaction of sulfides with alkyl hydrogen sulfates (or alcohols and sulfuric acid) (7). It seemed of interest to examine this reaction for evidence of rearrangement.

The reaction between dimethyl sulfide, benzyl alcohol, and sulfuric acid in glacial acetic acid resulted in the isolation of the normal product as $2C_7H_7(CH_3)_2SCl \cdot BiCl_3$. Due, possibly, to the low boiling point of the methyl sulfide no rearrangement occurred.

Benzyl sulfide, methyl alcohol, and sulfuric acid in glacial acetic acid, however, yielded tribenzylsulfonium sulfate. Rearrangement occurs, therefore, both with dimethyl sulfate and methyl hydrogen sulfate. It is possible that tribenzylsulfonium sulfate and benzyldimethylsulfonium sulfate are more stable than the other possible compounds, trimethylsulfonium sulfate and dibenzylmethylsulfonium sulfate, which were not isolated. These latter may have been present in small amounts in the gummy residues that could not be crystallized.

Due to the delitescent character of the sulfonium sulfate equilibrium our experiments are not as complete as they were with the sulfonium halides. They, nevertheless, leave no doubt that a similar series of equilibria exists. Limiting ourselves to the data secured we may summarize this as follows.

IV



$$\begin{tikzcd}
\underset{A}{RSR} + \underset{B}{(CH_3)_2SO_4} \arrow[dr, leftrightarrow] & \\
& \underset{C}{R_2CH_3SSO_4CH_3} \arrow[dl, leftrightarrow] \\
\underset{D}{RSCH_3} + \underset{E}{RSO_4CH_3} &
\end{tikzcd}$$

The reaction of A with E can then give $R_3SSO_4CH_3$ while the reaction of D with B results in $R(CH_3)_2SSO_4CH_3$.

EXPERIMENTAL PART

Trimethylsulfonium sulfate. Six and seven-tenths grams (0.053 mole) of dimethyl sulfate was mixed with 4.4 g. (0.071 mole) of dimethyl sulfide and the solution was cooled in an ice-bath. The reaction was quite vigorous and in a short while the trimethylsulfonium methyl sulfate solidified. It was extremely deliquescent and could not be isolated in a pure state. It was converted to the sulfate by hydrolysis with water and a clear solution was obtained.

Tris-trimethylsulfonium chloride-bis-bismuth chloride. To 71 cc. of an aqueous solution of trimethylsulfonium sulfate (0.02 mole) was added 61.4 cc. (0.02 mole) of normal bismuth chloride. The mixture was stirred during the addition and a small precipitate of bismuth oxychloride was discarded. The filtrate on evaporation gave beautiful glistening white prisms. On recrystallization from dilute hydrochloric acid they decomposed at 245°. Analyses for carbon, hydrogen, sulfur, bismuth, and chlorine showed it to be $3(CH_3)_3SCl \cdot 2BiCl_3$.

Anal. Calc'd for $C_9H_{37}Bi_2Cl_9S_3$: C, 11.15; H, 2.79; S, 9.92; Bi, 43.17; Cl, 32.97.
Found: C, 11.3 (11.16[3]); H, 2.44 (2.75[3]); S, 10.03; Bi, 43.45; Cl, 32.75 (32.49[3]).

The identical compound was obtained when trimethylsulfonium chloride was treated with an equimolar amount of bismuth chloride. The trimethylsulfonium chloride was prepared from the iodide by treatment first with silver oxide followed by neutralization with hydrochloric acid.

Trimethylsulfonium chloride-bismuth chloride. When 0.15 mole of trimethylsulfonium sulfate was treated with 0.20 mole of bismuth chloride as described above, white crystals melting at 121–123° were obtained which proved to be $(CH_3)_3SCl \cdot BiCl_3$.

Anal. Calc'd for $C_3H_9BiCl_4S$: S, 7.48. Found: S, 7.24.

Equal moles of benzyl sulfide and dimethyl sulfate. A benzene solution of 21.4 g. (0.1 mole) of benzyl sulfide and 12.6 g. (0.1 mole) of dimethyl sulfate was heated on the water-bath for 14 hours. Water (100 cc.) was then added and the mixture was again heated for seven hours or until the hydrolysis was complete. The dark colored benzene layer was separated and on evaporation deposited crystals of benzyl sulfide. The clear, colorless aqueous layer was treated with bismuth chloride (100 cc. of 3 *N*). Hydrochloric acid was added until a clear solution was obtained, a total of 300 cc. of 6 *N* HCl being used. A small amount of gummy precipitate was discarded. The filtrate, on evaporation, gave a white precipitate which was recrystallized from diethyleneglycol monoethyl ether (Carbitol) by the addition of acetone. After several such purifications it melted constantly at 140° and decomposed at 145°. Analysis showed it to be $3(CH_3)_2C_7H_7SCl \cdot 2BiCl_3$.

Anal. Calc'd for $C_{27}H_{39}Bi_2Cl_9S_3$: S, 8.03; Bi, 34.94.
Found: S, 7.98; Bi, 35.2.

Two moles of benzyl sulfide to one of dimethyl sulfate. A solution of 21.4 g. (0.1 mole) of benzyl sulfide and 6.3 g. of dimethyl sulfate (0.05 mole) in 200 cc. of glacial acetic acid was heated for three hours, and then most of the acetic acid was removed under vacuum. The residual liquor was poured into water. An oil and a solid separated. The oil was soluble in benzene and was benzyl sulfide. The solid was recrystallized from very dilute sulfuric acid. It melted at 173° and proved to be tribenzylsulfonium sulfate. Fichter and Sjöstedt (7) give 170–175°. A mixed melting point with authentic material prepared by Fichter and Sjöstedt's method showed no depression.

Anal. Calc'd for $C_{21}H_{22}O_4S_2$: S, 15.92. Found: S, 16.03.

Benzyl sulfide, methyl alcohol, and sulfuric acid. A solution of 13.1 g. (0.06 mole) of benzyl sulfide in 150 cc. of glacial acetic acid was heated with 10 cc. of concentrated sulfuric acid and 2.5 cc. (0.06 mole) of absolute methyl alcohol for two hours. Most of the glacial acetic acid was removed in a vacuum and the residual liquor then separated into two layers. The upper layer proved to be benzyl sulfide. The lower layer was treated with water and a white solid precipitated. On recrystallization from very dilute sulfuric acid it melted at 174° and proved to be tribenzylsulfonium sulfate.

Methyl sulfide, benzyl alcohol, and sulfuric acid. A solution of 3.7 g. (0.06 mole) of methyl sulfide, 6.5 g. (0.06 mole) of benzyl alcohol, and 10 cc. of concentrated sulfuric acid in 150 cc. of glacial acetic acid was allowed to stand at room temperature for 12 days. The acetic acid was removed as described previously and the residue treated with water. An oil separated which was insoluble in ether. It was dissolved in acetic acid and bismuth chloride was added. The precipitate seemed to be a mixture, as it melted indefinitely between 89° and 130°. On recrystallization from dilute hydrochloric acid, however, a crystalline com-

---

[3] Analyses by Carl Tiedke.

pound was obtained that melted at 138°. On analysis it proved to be $2C_7H_7(CH_3)_2SCl \cdot BiCl_3$, showing that no rearrangement had occurred.

Anal. Calc'd for $C_{18}H_{26}BiCl_5S_2$: C, 31.2; H, 3.8; S, 9.25; Bi, 30.18.
Found: C, 31.06; H, 3.43; S, 9.00; Bi, 30.54.

Analytical notes. No difficulty was experienced in the analysis for C and H, or for sulfur by either the Carius or Parr bomb methods. Bismuth gave considerable trouble until the method of Myttenaere (22) was somewhat modified as follows. A sample of 0.5 g. was mixed with 4 g. of 1:2 potassium nitrate-potassium carbonate and 10 cc. of water in a platinum dish. This was carefully evaporated to dryness on the water-bath, cautiously heated and finally ignited at a temperature of 450–500°. The *cooled* melt should be yellow. When the cooled melt was orange in color, inaccurate results were obtained. Further heating was necessary. Water was then added to disintegrate the melt and the precipitate was filtered, washed until neutral and ignited. If filter paper was used, a few drops of nitric acid was added to convert any reduced bismuth to Bi_2O_3.

SUMMARY

The reaction between benzyl sulfide and dimethyl sulfate and between benzyl sulfide and methyl hydrogen sulfate has been shown to result in rearranged products, tribenzylsulfonium sulfate and benzyldimethylsulfonium sulfate. The latter was isolated as $3C_7H_7(CH_3)_2SCl \cdot 2BiCl_3$·

The mechanism proposed by Ray and Levine for the formation of sulfonium halides has been extended to the sulfonium sulfate.

No rearrangement was observed when dimethyl sulfide reacted with benzyl hydrogen sulfate.

CINCINNATI, OHIO.

REFERENCES

(1) Part I. RAY AND LEVINE, *J. Org. Chem.*, **2**, 267 (1937).
(2) MÜLLER AND SCHÜTZ, *Ber.*, **71**, 692 (1938).
(3) BOST AND SCHULTZE, *J. Am. Chem. Soc.*, **64**, 1165 (1942).
(4) CRUM-BROWN AND BLAIKE, *J. prakt. Chem.*, [2], **23**, 395 (1881).
(5) KEHRMANN AND DUTTENHÖFER, *Ber.*, **38**, 4197 (1905).
(6) RÂY AND RÂY, *J. Indian Chem. Soc.*, **4**, 37 (1927).
(7) FICHTER AND SJÖSTEDT, *Ber.*, **43**, 3422 (1910).
(8) ZINCKE AND GLAHN, *Ber.*, **40**, 3039 (1907).
(9) SMILES AND HILDITCH, *J. Chem. Soc.*, **93**, 150 (1908).
(10) KEHRMANN, LIEVERMANN AND FRUMKINE, *Ber.*, **51**, 474 (1918).
(11) RICHTER, *Ann.*, **416**, 291 (1918).
(12) LIBERMANN, *Compt. rend.*, **198**, 1421 (1934).
(13) LUTTRINGHAUS AND HAUSCHILD, *Ber.*, **72**, 887 (1939).
(14) Patents: Brit., 434,810 (1935); 466,734 (1937); 464,330 (1937); 525,237 (1940); 535,490 (1941); 535,468 (1941); Can., 388,120 (1940); Dutch, 47,897 (1940); Fr., 807,213 (1937); 810,437 (1937); 840,778 (1939); Ger., 700,847 (1940), 705,224 (1941); U.S.A., 2,094,090 (1937); 2,193,963 (1940); 2,204,976 (1940); 2,230,587 (1941).
(15) AUWERS AND ARNDT, *Ber.*, **42**, 2713 (1909).
(16) BRAND AND STALLMANN, *Ber.*, **54**, 1578 (1921).
(17) Part II. RAY AND SZASZ, *J. Org. Chem.*, **8**, 121 (1943).
(18) VANINO AND MUSSGNUG, *Ber.*, **50**, 23 (1917).
(19) BLATTLER, *Monatsh.*, **40**, 417 (1919).
(20) JÖRGENSEN, *Ber.*, **2**, 460 (1869).
(21) KRAUT, *Ann.*, **210**, 310 (1882).
(22) MYTTENAERE, *J. pharm. Belg.*, **11**, 449 (1929).