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I hereby recommend that the thesis prepared under my supervision by Josselyn Liszniewska Farmer *entitled* Sulfonium Compounds. The Reaction of Organic Sulfides with Organic Sulfates.

be accepted as fulfilling this part of the requirements for the degree of Ph. D

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S U L F O N I U M C O M P O U N D S

The Reaction of Organic Sulfides with Organic Sulfates

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by

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For the unfailing encouragement and generous kindliness of Dr. Ray, who assisted in the nurture of this brainchild of his, the author wishes to express her esteem and heartfelt appreciation.

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PART I:

INTRODUCTION

Sulfonium Compounds

In 1864 von Oefele discovered a new type of organic sulfur compound, containing a tetravalent sulfur atom. The name he originally gave to these compounds, which he called "sulfinbasen", was later changed to sulfonium bases, to indicate their resemblance to the organic ammonium bases.

Oefele (1) found that diethyl sulfide would react with ethyl iodide, on warming in presence of water, to give triethylsulfonium iodide, according to the following equation.

$$Et_2S + EtI \longrightarrow Et_3SI$$

The work that followed Oefele's discovery showed that this reaction is not as simple as it would appear. Not only was it found that, as the molecular weight of the reactants increases, the reaction proceeds much more slowly or not at all (2), but also that in some cases the compounds that should logically be produced could not be isolated. For example, Cahours (3) attempted to make dibenzylmethylsulfonium iodide from the interaction of dibenzyl sulfide and methyl iodide, but was able to obtain only trimethylsulfonium iodide. Schöller (4) carried out the same

reaction at a lower temperature and succeeded in obtaining benzyldimethylsulfonium iodide, but he also was unable to isolate any dibenzylmethylsulfonium iodide.

In 1937, Ray and Levine (5) proposed a new mechanism for the sulfonium reaction, thereby offering a satisfactory explanation for the general formation of trimethyl or triethylsulfonium iodide in the interaction of higher alkyl sulfides with methyl or ethyl iodide. It was shown that there is a temporary formation of the desired sulfonium compound,

$$R_2S + MeI \rightleftharpoons R_2SMeI$$

followed by the establishment of a series of equilibria, in the course of which other sulfides are produced. These then can react further with the alkyl halide, the ultimate product of these equilibria being the sulfonium salt containing the simplest alkyl radical.

$$R_2SMeI \rightleftharpoons RSMe + RI$$

$$RMeS + MeI \rightleftharpoons RMe_2SI$$

$$RMe_2SI \rightleftharpoons Me_2S + RI$$

$$Me_2S + MeI \rightleftharpoons Me_3SI$$

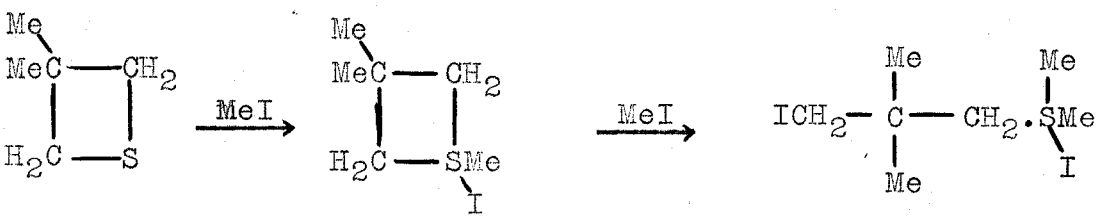
This mechanism has been quite recently borne out by the work of Muller and Schütz (6). These authors, in an

investigation of polymembered cyclic rings, prepared tetradecamethylene sulfide. The sulfide was analysed with methyl iodide, producing trimethylsulfonium iodide and 1,14-diiodotetradecane as follows:

$$(CH_2)_{14}S \xrightarrow{MeI} (CH_2)_{14}S.MeI \xrightarrow{2MeI} Me_3SI + (CH_2)_{14}I_2$$

Thus a sulfonium compound of a cyclic sulfide was first obtained, followed by the breaking of the ring, with the formation of trimethylsulfonium iodide.

A similar reaction had been reported in 1934 by Becker and Keuning (7), who found that, in the interaction of methyl iodide with 3,3-dimethylthiocyclobutane, the ring was broken. The product obtained was 3-iodo-2,2-dimethylpropyldimethylsulfonium iodide,



showing that the equilibrium had not proceeded to the formation of trimethylsulfonium iodide because the molar ratio used was 0.01 mole of the thio ether to 0.022 mole of methyl iodide, or approximately 1 : 2. Had the ration been 1 : 3, as in the example previously cited, the formation of tri-

methylsulfonium iodide could have been expected.

The difficulties encountered by Scholler and Cahours in their attempts to prepare mixed sulfonium compounds were obviated by Hilditch and Smiles (8) in 1907, by the use of mercuric iodide, by means of which they obtained dibenzylmethylsulfonium iodide. Smiles (9) had found, earlier, that the addition of mercuric iodide to a mixture of an alkyl sulfide and an alkyl iodide hastened the formation of the sulfonium iodide. The mercuric iodide apparently reacts first with the sulfide, forming an addition compound

$$R_2S + HgI_2 \longrightarrow R_2S.HgI_2$$

which then reacts with the iodide

$$R_2S.HgI_2 + RI \longrightarrow R_3S.HgI_3$$

to form the mercuric iodide double salt. The seemingly catalytic effect of the mercuric halide may be simply a result of the fact that its presence stabilizes the sulfonium compound, making its redissociation less likely to occur. That even these mercuric double salts dissociate is indicated by the recent work of Haas and Dougherty (10) who studied the reaction of alkyl disulfides with benzyl iodide in the presence of mercuric iodide. Following the mechanism proposed by Steinkopf and Muller (11) for the reaction of alkyl disulfides with alkyl halides, these workers postulate that

the following reactions occur:

1) $R\text{-}S\text{-}S\text{-}R + HgI_2 + C_7H_7I \longrightarrow R\text{-}S(C_7H_7I)\text{-}S\text{-}R.HgI_2$

2) $R\text{--}S(C_7H_7I)\text{--}S\text{--}RHgI_2 \longrightarrow C_7H_7SR.HgI_2 + RSI$

3) $C_7H_7.S.RHgI_2 + C_7H_7I \longrightarrow (C_7H_7)_2RSI.HgI_2$

4) $RSI + C_7H_7I \longrightarrow C_7H_7RS.I_2$

5) $C_7H_7RS.I_2 + HgI_2 \longrightarrow C_7H_7RS.HgI_2 + I_2$

6) $C_7H_7SRHgI_2 + C_7H_7I \longrightarrow (C_7H_7)_2RSI.HgI_2$

7) $R\text{-}S\text{-}S\text{-}R + 4\ C_7H_7I + 2\ HgI_2 \longrightarrow 2\ (C_7H_7)_2RSI.HgI_2 + I_2$

Haas and Dougherty here used the old method of writing the formulae for the double salts. Since Cavel and Sugden (12) and Ray and Adhikari (13) have found that they dissociate into the sulfonium ion and the mercury triiodide ion, $R_3S^+ + HgX_3^-$, these salts are generally written R_3SHgI_3.

Most of the work that followed Oefele's discovery of sulfonium compounds was limited to the iodides. In general, any other derivatives prepared were converted to the iodide or else isolated as double salts with metallic salts. The failure of alkyl halides to react with sulfides in

which the sulfur is directly bound to an aromatic nucleus led to the belief that such compounds could not exist. In 1905, however, Kehrmann and Duttenhofer (14) opened the way to the production of numerous aromatic sulfonium compounds by their discovery that aromatic sulfides did react with alkyl sulfates to form sulfonium sulfates.

PART II:

DISCUSSION

It is possible that an equilibrium similar to the halide equilibrium (5) exists for the sulfonium sulfates. If such an equilibrium exists, the interaction of a complex sulfide with methyl sulfate should ultimately lead to the production of trimethylsulfonium sulfate. Nevertheless, although many cases can be cited as evidence for the halide equilibrium(15), a search of the literature revealed not a single suggestion that such an equilibrium exists for the sulfonium sulfates.

This lack of evidence in the case of the sulfates might be partially explained by the fact that, if trimethylsulfonium sulfate was produced in these reactions, it was probably present in only small amounts, and since, unlike the iodide, it is extremely soluble and hygroscopic, it might well have escaped detection.

The purpose of the present investigation is to determine if such an equilibrium does in fact exist.

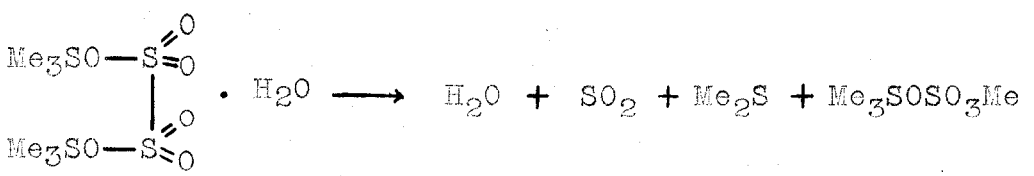
Trimethylsulfonium sulfate is not frequently referred to in the literature. The earliest reference to trimethylsulfonium salts is found in the work of Cahours (16), who described trimethylsulfonium hydroxide and mentioned that the base gives well-defined crystalline salts on reaction with acids. It is possible that he prepared the sul-

fate, but he makes no specific reference to sulfuric acid, and, since trimethylsulfonium sulfate is hardly what could be called a well-defined salt, it appears unlikely that Cahours obtained the sulfate.

Oefele (1) had previously prepared the corresponding triethylsulfonium hydroxide, from which he obtained the chloride, the sulfate, and the oxalate by neutralization. He stated that the salts were readily formed, but extremely hygroscopic, and beyond that said no more about them.

In 1865, Dehn (17) claimed to have prepared bis-triethylsulfonium sulfate from the corresponding chloride and silver sulfate. He described the salt as readily soluble in water, difficultly so in strong alcohol, and little hygroscopic when pure. No analyses were given and there is a possibility that the salt was a double salt.

The next reference to trimethylsulfonium sulfate was made by Crum-Brown and Blaikie (18) in 1881. These authors claim to have prepared trimethylsulfonium methylsulfate from the decomposition of the dithionate:



The trimethylsulfonium methylsulfate proved to be deliquescent and soluble in water and alcohol. Consequently it

was identified by the production of trimethylsulfonium iodide on treatment of a solution of the salt with potassium iodide, and by the precipitation of barium sulfate from the filtrate.

In 1927, Rây and Rây (19) prepared a series of salts of triethylsulfonium sulfate, obtained only in solution, and sulfates of metals in the copper-magnesium group. These were deliquescent and allegedly contained 10 or 11 molecules of water of crystallization, but some variations in the analyses make the exact amount of water of crystallization uncertain. The same workers (20) obtained a similar series the following year from a solution of trimethylsulfonium sulfate, and although these salts were found to be less hygroscopic, their solubility and somewhat indefinite composition were such as to make them of doubtful value for the isolation of trimethylsulfonium sulfate from a solution containing other substances.

Although Rây and Rây stated, in 1927, (19) that "sulfonium sulfates have not yet been isolated", the first sulfonium sulfate was isolated as early as in 1910. In that year Fichter and Sjösted (21) prepared tribenzylsulfonium sulfate during the electrolytic oxidation of benzyl sulfide in concentrated sulfuric acid and glacial acetic acid. The mechanism for the reaction was postulated as follows:

oxidation of the sulfide to the sulfinic acid

$$(C_7H_7)_2S + O_2 + H_2O \longrightarrow C_7H_7SO_2H + C_7H_7OH$$

and further reaction of the benzyl alcohol produced with benzyl sulfide and sulfuric acid, to give tribenzylsulfonium sulfate:

$$(C_7H_7)_2S + C_7H_7OH + H_2SO_4 \longrightarrow (C_7H_7)_3SSO_4H + H_2O$$

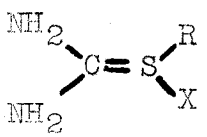
Fichter and Sjöstedt also prepared this sulfate from benzyl sulfide, benzyl alcohol, and sulfuric acid, in glacial acetic acid and from tribenzylsulfonium chloride ferric chloride, by first removing the iron with ammonium hydroxide, filtering, and treating the iron-free solution with saturated ammonium sulfate solution and excess sulfuric acid.

Still earlier, in 1907, Zincke and Glahn (22) claimed the preparation of a sulfonium sulfate of anhydro-2,6-dinitrophenol 4-dimethylsulfonium, from the base and sulfuric acid in alcoholic or glacial acetic acid solution. They described the salt as colourless and remarked that it was decomposed immediately by water, but no further data such as melting point or analyses were given.

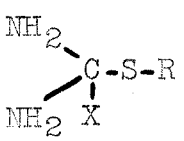
In 1908, Smiles and Hilditch (23) had prepared S-phenetyl-3, 3'-dinitrophenazothionium sulphate from di-p-nitrodiphenylamine sulfoxide and phenetole in concen-

trated sulfuric acid. The salt, formed in almost theoretical yield, was bluish green, bright green after drying on a porous plate in a vacuum, and dark blue after drying at 100°. The salt was not analysed but converted to the base, from which other derivatives were prepared. Kehrmann, Lievermann, and Frumkine (24) obtained the same compound as light straw-yellow prisms and claimed that Smiles had isolated impure materials. These investigators also converted the sulfate to other derivatives, so that there is no further positive information about these sulfates, other than their colour.

Taylor (25), in 1917 reacted thio-carbamide with alkyl sulfates and concluded that the compounds formed were sulfonium compounds (a) since they acted as salts of strong bases. He considered the two other possible structures (b and c) as unlikely.



a)



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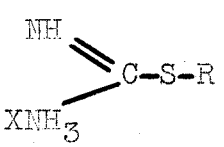
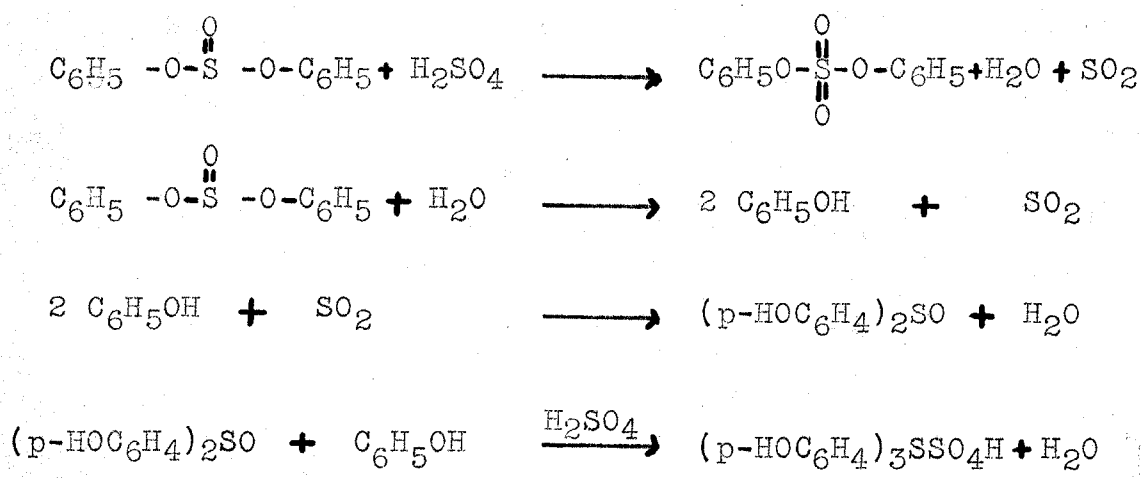


c)

Libermann (26), in 1934 prepared o,o',o''-trihydroxytritolylsulfonium chloride from the action of thionyl chloride on orthocresol,

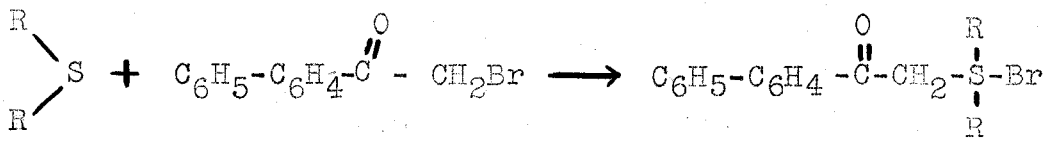
and treated it with alcoholic sodium cyanide to obtain the free base. He prepared o,o',o''-trihydroxytritolylsulfonium sulfate from this base and sulfuric acid and declared that it was identical with the supposed sulfate of a triaryl-orthosulfurous acid of Richter (27). The latter had obtained the compound in question by the reaction of a neutral aryl sulfite with concentrated sulfuric acid. The reaction probably takes place as follows:



In 1939, Luttringhaus and Hauschild (28) obtained a neutral salt, p,p',p''-trihydroxytriphenylsulfonium sulfate, by treating the corresponding sulfonium chloride with 5% sulfuric acid in acetic acid solution.

Bost and Schultze (29), in 1942, made a series of sulfonium sulfates from dialkyl-p-phenylphenacylsulfonium bromides with silver sulfate. The purpose of the research was to determine whether p-phenylphenacylbromide was a

suitable reagent for the identification of alkyl sulfides and the results were very satisfactory. This reagent adds readily to the sulfides as shown in the accompanying equation.



In this series, the authors prepared the bisulfates of the diethyl, dipropyl, dibutyl, methylethyl, methylpropyl, and methylbutyl compounds. The dimethyl compound alone gave a normal sulfate.

That the preparation of these compounds is not a matter of purely academic interest is illustrated by the number of patents that have been taken out during the last seven years for the use of sulfonium sulfates and methylsulfates. It is claimed that these are of value as wetting, foaming, and emulsifying agents; cleansing, dispersing, and stripping agents; disinfectants and fungicides; and agents to improve the fastness of dyes. Dyes themselves may be obtained from the interaction of phthalocyanins with dimethyl sulfate. There are many patents that, with the mystery characteristic of the art, do not specify the exact nature of the product, or else do not divulge the method of pre-

paration of the compounds obtained. Consequently, I have restricted myself to such patents as contain direct mention of the use of either the sulfonium sulfate or methyl sulfate. A list of these can be found in table I (page 15).

It is interesting to note that the sulfonium sulfates that have been isolated up to this time have most generally been prepared by the neutralization of the sulfonium base, or by the interaction of a sulfonium halide with silver sulfate. In the numerous cases in which an organic sulfide was caused to react with methyl sulfate, the sulfonium compound was either isolated as such, when this was feasible, or else converted to a double salt with some metal salt.

The earliest isolation of a sulfonium methylsulfate was accomplished in 1909, by Auwers and Arndt (47), who isolated dimethyl-p-cresylsulfonium methylsulfate from the reaction between p-thiocresol and dimethyl sulfate. The salt was described as easily soluble in water, alcohol, and chloroform. Auwers and Arndt stated that it was stable in water and, recrystallized from absolute alcohol by precipitation with ether, melted at 97°. The methyl-sulfate obtained from the interaction of p-tolylethyl sulfide and dimethyl sulfate was an oil which, on distillation, gave p-tolylmethyl sulfide. It is interesting to note here also that

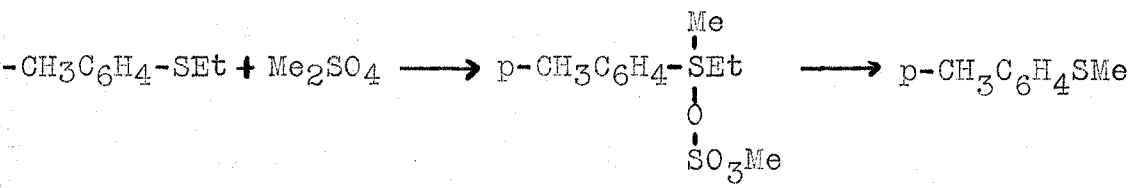
TABLE I **Patents on Sulfonium Sulfates or Methosulfates**

Ref.	Types of Compounds	Preparation	Uses
(30)	methylethylcetylsulfonium methylsulfate	sulfonium base + Me_2SO_4	stripping agent
(31) & (41)	$(R')_2S\ AC - R - S(Ac)(R')_2$ R' = Me, Et, or C_7H_7 R = at least 10 carbon atoms Ac = $\frac{1}{2}\ SO_4$ or other anion	disulfide + Me_2SO_4	wetting, foaming, or emulsifying agents. Also to improve fastness of dyes.
(32)	octadecyldimethylsulfonium methylsulfate	sulfide + Me_2SO_4	wetting, cleansing, and dispersing agents. Also for use in dye industry.
(33)	dodecylbenzylmethylsulfonium methylsulfate didecyl " " " dodecyl-p-tolyl " " "	thioether + Me_2SO_4	disinfectants and fungicides
(34)	diisooctylmethylsulfonium methylsulfate	sulfide + Me_2SO_4	disinfecting and preserving agents
(35)	octadecylbenzothiazolylmethylsulfonium methylsulfate	2 octadecylmercaptobenzothiazole + Me_2SO_4	emulsifying, softening, and detergent agents
(36)	dimethylcetylsulfonium methylsulfate	thio ether, saturated primary alcohol and H_2SO_4	wetting and emulsifying agents
(37)	$R_1R_2R_3S\ X$ R_1 = lipophylic radical R_2 & R_3 = alkyl, aryl, aralkyl, cyclic, heterocyclic or alkylol X = anion, may be HSO_4	- - - - - -	wetting, emulsifying, and detergent

Table I (Patents on Sulfonium Sulfates or Methosulfates (cont'd))--

(38)	sulfonium sulfates	thio ether and saturated primary alcohol with H_2SO_4	foam-forming, emulsifying, and wetting agents
(39) & (40)	sulfonium sulfates dimethylcetylsulfonium methylsulfate	same as (38)	capillary active sulfonium sulfates
(42)	hexadecylethylmethylsulfonium methylsulfate 2,6-dichlorobenzyldecylmethylsulfonium methylsulfate	- - - - - -	disinfectants against B. coli, B. typhus, B. diphtheria, staphylococci
(43)	sulfonium methylsulfates	alkyl or aralkylmercaptophthalocyanins + Me_2SO_4	direct dyes for cotton and viscose rayon
(44)	sulfonium sulfates	thio ether and saturated monohydric primary alcohol with sulfuric acid	wetting, emulsifying, and foaming agents
(45) & (46)	sulfonium sulfates	sulfuric acid ester of primary aliphatic alcohol of low molecular weight and thio ether	- - - - -

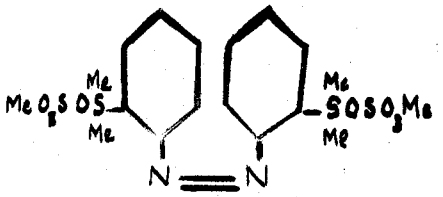
the sulfonium compound obtained in the reaction, on distillation, dissociated with the formation of a different sulfide.



The mechanism of Ray and Levine (5) can also be applied here, to explain the formation of p-tolylmethyl sulfide.

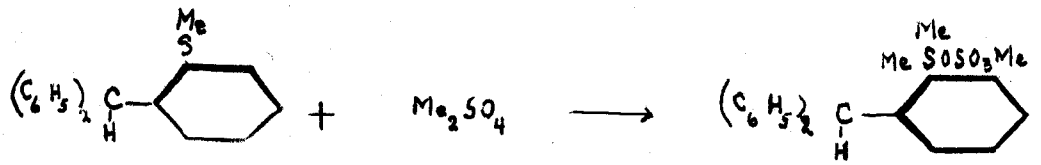
The next sulfonium methylsulfate was reported in 1921. In that year, Brand and Stallmann (48) reacted o-nitrophenylmethyl sulfide with dimethyl sulfate and obtained o-nitrophenyldimethylsulfonium methylsulfate as colourless, stout crystals, decomposing at 155-7°. The compound yellowed on long standing and Brand and Stallmann remarked that the decomposition probably gave the original sulfide.

In 1923, Brand and Grobel (49) obtained o,o'-azophenyldimethylsulfonium methylsulfate in almost quantitative yield from o,o'-azophenylmethyl sulfide and dimethylsulfate.

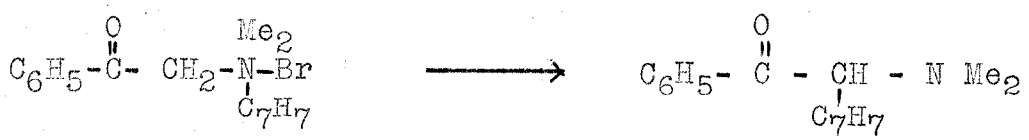


The crystals that formed were yellow to orange and melted to a red liquid at 189°. The corresponding azoxy compound, which turned red at 161-2° and melted at 167-9°, with the evolution of a gas (bath, 150°), was found to be decomposed by water.

The following year, Brand and Stallmann (50) isolated another sulfonium methylsulfate from a reaction between o-methylmercapto-triphenylmethane and dimethylsulfate. The salt when recrystallized from alcohol melted at 163°.

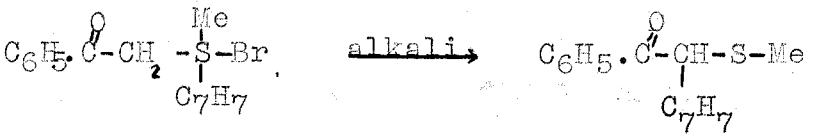


A rather remarkable reaction was reported in 1932 by Thomson and Stevens (51). It was previously known that if certain organic ammonium bromides were treated with alkali, a molecular rearrangement occurred (52)(53). For example, if phenacylbenzyldimethylammonium bromide is treated with alkali, ω-benzyl-ω-dimethylaminoacetophenone is produced as follows:



Evidently hydrogen bromide splits off and the benzyl radical shifts to the carbon atom that has lost one

hydrogen atom. Thomson and Stevens were curious to see whether the same reaction would take place with a sulfonium compound, so they treated phenacylbenzylmethylsulfonium bromide with alkali and obtained ω.benzyl-ω-methylthiol-acetophenone, showing that an analogous reaction had taken place.



The structure of the product was proved by treating it with dimethylsulfate. The oily sulfonium salt obtained was reduced with zinc dust and sulfuric acid, and the sulfonium compound was destroyed. Benzylacetophenone resulted, indicating that the benzyl group had been transferred from the sulfur atom to the adjacent carbon atom. Here also it is quite possible that trimethylsulfonium sulfate may have been produced, but there is no evidence to support such an assumption.

From the preceding description of the various sulfonium sulfates and methylsulfates it can be seen that, in such cases as would have permitted the formation of sulfonium sulfates other than that expected, no one has yet reported the isolation of any other than the normal products.

In our investigation, we have attempted to discover whether some evidence could be found for the existence

of an equilibrium similar to that of the sulfonium halides.

PART III:

Procedure:

Before attempting to see whether trimethylsulfonium sulfate might be produced in the interaction of an organic sulfide other than methyl sulfide with dimethyl sulfate, it was necessary to find some satisfactory means of isolating and identifying it.

Several attempts were made to convert trimethylsulfonium sulfate to the picrate. Although the picrate can be readily formed from sulfonium halides with sodium picrate, difficulties were encountered when trimethylsulfonium sulfate was treated with sodium picrate or with picric acid. Addition of organic or inorganic bases to neutralize the sulfuric acid resulted in the preferential precipitation of the picrates of the bases and in contamination of the small quantities of sulfonium picrate isolated. The formation of two different picrates, the normal picrate, and a low-melting picrate that analysed for the normal picrate with two moles of picric acid, further discouraged the use of this reagent.

There remained two possibilities: (a) the conversion of the sulfate to the corresponding iodide, and (b) the formation of some double salt. The former method

would result in the establishment of the halide equilibrium, and would prove nothing about a possible sulfate equilibrium. Consequently, the only choice lay in the selection of the metallic salt which might conveniently and satisfactorily be used for the isolation of trimethylsulfonium sulfate.

The isolation of sulfonium salts has been most commonly achieved by precipitation as double salts with platinum and mercury salts, less often with salts of gold, silver, copper, bismuth, cadmium, magnesium, zinc, arsenic, antimony, manganese, iron, lead, and tin (54).

The mercuric salts, which seem to have been more widely used than any, are formed in such a wide variety of ratios (55) that it was deemed wiser to select some other precipitant.

An attempt to prepare a bismuth iodide double salt, from solutions of the sulfonium sulfate and potassium bismuth tetraiodide, gave a compound that could be recrystallized only with difficulty (56). Blättler (57) had prepared a bismuth iodide double salt of trimethylsulfonium iodide and claimed that it did not melt below 290°. The compound I obtained decomposed sharply at 220° when heated rapidly; so it is possible that her material was contaminated with inorganic material. Blättler also prepared a double salt of bismuth bromide with trimethylsulfonium bromide

and found that it contained one mole of bismuth bromide to two moles of the sulfonium bromide. The iodide she had obtained was in a 1 : 1 ratio. Naturally, she prepared the analogous chloride of the sulfonium chloride, but here also she probably had an impure compound. She gave no melting point and her analytical results were so inconclusive that she did not even assign a formula to the salt.

In 1917, Vanino and Mussgnug (58) had prepared a double salt of trimethylsulfonium iodide with bismuth chloride. The salt had a definite melting point and could be readily recrystallized from dilute hydrochloric acid. In the hope that I might obtain a similar salt of the sulfonium sulfate with bismuth chloride, I precipitated the sulfonium sulfate solution with bismuth chloride. The compound that I obtained, on recrystallization from dilute hydrochloric acid, was in the form of white, glistening crystals, decomposing at 245° with ebullition. It was shown by analyses for carbon, hydrogen, bismuth, sulfur, and chlorine, to consist of three molecules of the sulfonium chloride to two molecules of bismuth chloride, $3\ Me_3SCl.\ 2\ BiCl_3$. The same compound was obtained by mixing equimolar quantities of solutions of trimethylsulfonium chloride and bismuth chloride. When an excess of bismuth chloride was used, a compound melting at 121° was obtained. An analysis for sulfur indicated that the salt was a 1 : 1

compound, $Me_3SCl.BiCl_3$.

Thus the only bismuth chloride salts referred to in the literature were the one prepared by Blättler and that of Vanino and Mussgnug. Jörgensen (59) prepared a double salt of triethylsulfonium bromide with bismuth bromide and assigned to it the formula $3Et_3SBr.2BiBr_3$. However, no analytical details were given. Kraut (60) prepared three bismuth iodide salts of triethylsulfonium iodide, but gave no melting point for any of them. Since one of them was claimed to be a 1 : 1 compound, $Et_3SI.BiI_3$, and the 1 : 1 compound I had prepared decomposed at 218°, it is possible that Kraut had obtained impure compounds. Kraut had obtained $Et_3SI.BiI_3$ from equimolar quantities of the two salts. Using an excess of the sulfonium iodide and potassium bismuth tetraiodide, he obtained a compound containing three moles of the sulfonium iodide to two moles of bismuth iodide, $3Et_3SI.2BiI_3$. When this salt was recrystallized from the mother liquor or from alcohol, its composition changed to $2Et_3SI.3BiI_3$. If an excess of bismuth iodide was used for the precipitation, Kraut claimed that a salt of the following composition, $2Et_3SI.3BiI_3.9H_2O$, was obtained.

It can be seen that the bismuth compounds do not provide an escape from the pitfalls provided by the mercury salts. I rather suspect that, when the other metallic dou-

ble salts have been investigated as thoroughly, they may all be found to form compounds in a number of different ratios.

It was proposed to study the reaction of benzyl sulfide with dimethyl sulfate to see if any evidence of a rearrangement could be found. Benzyl sulfide was selected partly for its semi-aliphatic character, and partly because its high molecular weight should facilitate differentiation of the products.

Having prepared a compound that could serve as a means of isolating and identifying the elusive trimethylsulfonium sulfate, the next step was to prepare other compounds whose formation would be possible in this reaction. It occurred to me that I could, perhaps, prepare a series of bismuth chloride double salts by starting with sulfonium sulfates of known composition. By comparing my products with the members of this series, I might thus arrive at some valid conclusions as to their composition.

Fichter and Sjöstedt (21) had made tribenzylsulfonium sulfate by reacting benzyl sulfide, benzyl alcohol, and sulfuric acid in glacial acetic acid solution, I. I reasoned that, starting with benzyl sulfide and methyl al-

$$\text{I.}\quad (C_7H_7)_2S + C_7H_7OH + H_2SO_4 \longrightarrow (C_7H_7)_3SSO_4H + H_2O$$

cohol, I should be able to make dibenzylmethylsulfonium sulfate, II. In a similar manner, I hoped to isolate ben-

II. $(C_7H_7)_2S + CH_3OH + H_2SO_4 \longrightarrow (C_7H_7)_2CH_3SSO_4H + H_2O$

zyldimethylsulfonium sulfate, III, and, on treating these

III. $(CH_3)_2S + C_7H_7OH + H_2SO_4 \longrightarrow (CH_3)_2C_7H_7SSO_4H + H_2O$

salts with bismuth chloride, to obtain identifiable double salts.

I first prepared tribenzylsulfonium sulfate according to the method of Fichter and Sjöstedt. The compound obtained from the interaction of benzyl sulfide, benzyl alcohol and sulfuric acid in glacial acetic acid, melted at 174° and analysed correctly for sulfur. Fichter and Sjöstedt give 170°-175° (dependent upon the rate of heating) for the melting point of tribenzylsulfonium sulfate (21).

An attempt to prepare benzyldimethylsulfonium sulfate by the same method gave an oily product. Consequently, the oil was redissolved in glacial acetic acid and treated with bismuth chloride. The crystals that were obtained, after purification, melted at 138°-140° (depending upon the rate of heating). Analyses for carbon, hydrogen, bismuth, and sulfur indicated that the normal product, $(CH_3)_2C_7H_7SSO_4H$, had been formed and converted by the bismuth chloride into a compound of the following composition: $2(CH_3)_2C_7H_7SCl.BiCl_3$.

Next I wanted to prepare a bismuth chloride salt of dibenzylmethylsulfonium sulfate as another reference com-

pound. However, the product resulting from the reaction of benzyl sulfide with methyl alcohol, under similar conditions, was a solid. On purification, this compound proved to be, not the product expected according to equation II, but a compound melting at 174°, and identical with the tribenzylsulfonium sulfate produced in the reaction between benzyl sulfide and benzyl alcohol. Obviously, a rearrangement had occurred here.

This rearrangement can be explained if we assume that the theoretical sulfonium sulfate is first produced. This sulfate then can dissociate to give the original reac-

$$(C_7H_7)_2S + CH_3OH + H_2SO_4 \rightleftharpoons (C_7H_7)_2CH_3SSO_4H + H_2O$$

tants or to produce benzylmethyl sulfide and benzyl hydro-

$$(C_7H_7)_2CH_3SSO_4H \rightleftharpoons C_7H_7SCH_3 + C_7H_7SO_4H$$

gensulfate. The latter can now combine with unreacted benzyl sulfide, to form tribenzylsulfonium sulfate. It is also

$$(C_7H_7)_2S + C_7H_7SO_4H \rightleftharpoons (C_7H_7)_3SSO_4H$$

quite possible that the benzylmethyl sulfide might combine with unreacted methyl hydrogensulfate to give benzyldimethylsulfonium sulfate. An attempt was made to isolate the bis-

$$C_7H_7SCH_3 + CH_3SO_4H \rightleftharpoons C_7H_7(CH_3)_2SSO_4H$$

muth chloride salt that might be expected here from the filtrate. The white, granular precipitate that formed melted at 45-60°, with ebullition at 80-90°. It was soluble in Carbitol, but came down as a gum from this solvent, as well as from all the other solvents tried. While it seems possible that the benzyldimethylsulfonium ion was actually present in the mixture, it was not possible, in this case, to isolate it in the form of a pure salt.

Having isolated a well-defined bismuth chloride salt from the interaction of methyl sulfide, benzyl alcohol, and sulfuric acid in glacial acetic acid, an attempt was made to see if any rearrangement occurred in the reaction between benzyl sulfide and dimethyl sulfate. The sulfide was dissolved in benzene, dimethyl sulfate added, and the mixture refluxed on the water bath for several days. Then water was added and the refluxing continued for another day. After separation of the mixture, the aqueous layer was treated with bismuth chloride. The white precipitate that formed, when filtered off, was found to be gummy in nature. It could not be recrystallized from dilute hydrochloric acid as it retained its gummy character in this medium. Since it seemed to be insoluble in most of the available solvents, the material was extracted, first, with benzene, then with alcohol, and finally with acetone. During the treatment with acetone the compound became decently crystalline and fin-

ally melted at 110-111° and decomposed at about 140°. Another unsuccessful attempt was made to recrystallize it from dilute hydrochloric acid. It dissolved quite readily in Carbitol. On the addition of acetone, a cloudiness developed, and white needles separated out on standing. On further purification by the same method, the compound finally melted at 140° and decomposed at 145°. It was analysed for bismuth and for sulfur and the values obtained agreed well with those required by the formula

$$3(CH_3)_2C_7H_7SCl \cdot 2BiCl_3$$

The composition of this salt indicates that a rearrangement must have occurred here also. The following equations would illustrate the possible formation of a monobenzyldimethylsulfonium salt in this reaction:

I. $(C_7H_7)_2S + (CH_3)_2SO_4 \rightleftharpoons (C_7H_7)_2CH_3SSO_4CH_3$

II. $(C_7H_7)_2CH_3SSO_4CH_3 \rightleftharpoons C_7H_7SCH_3 + C_7H_7SO_4CH_3$

III. $C_7H_7SCH_3 + (CH_3)_2SO_4 \rightleftharpoons C_7H_7(CH_3)_2SSO_4CH_3$

The product of equation III, on addition of water, would be hydrolysed, forming the corresponding sulfonium sulfate. With bismuth chloride, the compound

$$3(CH_3)_2C_7H_7SCl \cdot 2BiCl_3$$

could be produced.

A question arises here. Why does the monobenzyldimethylsulfonium salt not dissociate further? Theoretically, the reactions shown by equations IV and V could take place and, if they occurred, trimethylsulfonium sulfate

IV. $C_7H_7(CH_3)_2SSO_4CH_3 \rightleftharpoons (CH_3)_2S + C_7H_7SO_4CH_3$

V. $(CH_3)_2S + (CH_3)_2SO_4 \rightleftharpoons (CH_3)_3SSO_4CH_3$

should be produced. It is possible that, under the conditions of the experiment, the benzyldimethylsulfonium methylsulfate is stable and that, if the mixture had ben subjected to more strenuous treatment, the other equilibria might have been established. The same question arises in the reaction between methyl sulfide, benzyl alcohol, and sulfuric acid, in which the normal product had been obtained. Since methyl sulfide is so volatile, the mixture had been allowed to stand, with no heating. It would be interesting to see whether, on heating, the following theoretical equilibria might not be established.

I. $(CH_3)_2S + C_7H_7OH + H_2SO_4 \rightleftharpoons (CH_3)_2C_7H_7SSO_4H + H_2O$

II. $(CH_3)_2C_7H_7SSO_4H \rightleftharpoons CH_3SC_7H_7 + CH_3SO_4H$

III. $CH_3SC_7H_7 + C_7H_7OH + H_2SO_4 \rightleftharpoons CH_3(C_7H_7)_2SSO_4H + H_2O$

IV. $CH_3(C_7H_7)_2SSO_4H \rightleftharpoons (C_7H_7)_2S + CH_3SO_4H$

V. $(C_7H_7)_2S + C_7H_7OH + H_2SO_4 \rightleftharpoons (C_7H_7)_3SSO_4H + H_2O$

Thus tribenzylsulfonium sulfate might eventually be produced and the methyl hydrogensulfate formed could react with the methyl sulfide present, giving trimethylsulfonium sulfate.

VI. $(CH_3)_2S + CH_3SO_4H \longrightarrow (CH_3)_3SSO_4H$

That only the normal product was isolated in this case may then also have been the result of conditions that were too mild to produce a rearrangement.

In addition, there is the possibility of obtaining one sulfonium compound in several different ratios with the bismuth chloride; and, if there is more than one sulfonium compound present, it is not difficult to imagine that a still more confusing series of mixtures may be formed. For instance, I am certain that the compound obtained in the reaction between benzyl sulfide and methyl sulfate, before the isolation of the final compound from Carbitol and acetone, was a mixture of $3(CH_3)_2C_7H_7SCl \cdot 2BiCl_3$ and some other salt, possibly the 2 : 1 compound, of whose composition I cannot yet be certain.

Since there was evidence that a rearrangement had occurred in the interaction of benzyl sulfide and dimethyl sulfate in benzene, I thought it would be interesting to see what products might be obtained if the same reaction were carried out in glacial acetic acid solution. In order to

favour the formation of tribenzylsulfonium sulfate, as shown in the following equation,

$$2(C_7H_7)_2S + (CH_3)_2SO_4 \rightleftharpoons (C_7H_7)_3SSO_4CH_3 + C_7H_7SCH_3$$

two moles of benzyl sulfide and one mole of dimethyl sulfate were heated to 70° in glacial acetic acid. The product isolated from this reaction was proved to be tribenzylsulfonium sulfate by a mixed melting point and sulfur analysis. So the rearrangement took place here also. Attempts to prepare a bismuth chloride salt from the filtrate gave a gummy solid that I found it impossible to crystallize.

It seemed logical that some other sulfide should be reacted with dimethyl sulfate or with methyl alcohol and sulfuric acid, to see whether evidence of rearrangement could be noted. Consequently n-butyl sulfide, methyl alcohol, and sulfuric acid were mixed in glacial acetic solution and allowed to stand for some time. The only product that was iso-

$$(C_4H_9)_2S + CH_3OH + H_2SO_4 \rightleftharpoons (C_4H_9)_2CH_3SSO_4H + H_2O$$

lated was a normal compound, as the bismuth chloride salt. It crystallized as flat, almost transparent plates, melting at 164° and carbon, hydrogen and sulfur analyses indicated that it had the composition $3(C_4H_9)_2CH_3SCl \cdot 2BiCl_3$. The material that precipitated first melted at a little over 150°. On recrystallization from dilute hydrochloric acid a

compound melting at 91° was obtained. This, on further recrystallization, gave the salt melting at 164°, so I suspect that the material melting at 91° was a 1 : 1 compound of the sulfonium chloride with bismuth chloride. There is comparatively little data on double salts to permit such a conclusion, but the mercuric iodide double salts of trimethylsulfonium iodide show that the 1 : 1 compound has a lower melting point than those containing other proportions of sulfonium iodide and mercuric iodide (55) and the cadmium iodide salts show the same relation (61). Also the 1 : 1 compound of trimethylsulfonium chloride with bismuth chloride, which I obtained by treating trimethylsulfonium sulfate with excess bismuth chloride, melted at 121°, whereas the 3 : 2 compound decomposed at 245°.

The reactions that were carried out and the products obtained are summarized in table II. It is clear that rearrangements occurred when benzyl sulfide was reacted with both dimethyl sulfate and methyl hydrogensulfate. These rearrangements may be explained by a mechanism that postulates the intermediate formation of the expected sulfonium sulfate, followed by dissociation and recombination until the most stable products are formed. In this case, it would seem that tribenzylsulfonium sulfate and benzyldimethylsulfonium sulfate are more stable than the intermediate dibenzylmethylsulfonium sulfate.

T A B L E I I

Reaction	Solvent	Products Isolated	Rearrangement
butyl sulfide and methyl-hydrogen sulfate	glacial acetic acid	$3(C_4H_9)_2CH_3SCl \cdot 2BiCl_3$	no
benzyl sulfide and dimethyl sulfate	benzene	$3C_7H_7(CH_3)_2SCl \cdot 2BiCl_3$	yes
benzyl sulfide and dimethyl sulfate	glacial acetic acid	$(C_7H_7)_3SSO_4H$	yes
benzyl sulfide, methanol and sulfuric acid	glacial acetic acid	$(C_7H_7)_3SSO_4H$	yes
methyl sulfide, benzyl alcohol and sulfuric acid	glacial acetic acid	$2C_7H_7(CH_3)_2SCl \cdot BiCl_3$	no

PART IV.

Experimental

A. Trimethylsulfonium salts

1. Trimethylsulfonium sulfate was prepared by mixing 6.7 grams (0.053 mole) of dimethyl sulfate and 4.4 grams (0.071 mole) of methyl sulfide in a glass-stoppered Erlenmeyer. The mixture was cooled in an ice bath, as the reaction was quite vigorous. The trimethylsulfonium methylsulfate that formed solidified very rapidly and was found to be extremely deliquescent. It was converted to trimethylsulfonium sulfate by the addition of 10 ml. of water and a clear solution was obtained.

a) Reaction with an equimolar quantity of bismuth chloride.

To 71 ml. of a solution of trimethylsulfonium sulfate (0.02 mole) was added 61.4 ml. (0.02 mole) of normal bismuth chloride. The mixture was stirred during the addition and a small amount of white precipitate formed. This was filtered off and dried, after which it was found to melt above 270°, so it was probably an inorganic bismuth salt. On evaporation of the filtrate, beautiful glistening white prisms separated out. After recrystallization from dilute hydrochloric acid, the compound decomposed at 245°, with ebullition. Analyses for carbon, hydrogen, sulfur, bismuth,

and chlorine showed that it was $3Me_3SCl \cdot 2BiCl_3$.

Anal.	Calculated for $C_9H_{27}S_3Bi_2Cl_9$:				
	C, 11.15;	H, 2.79;	S, 9.92;	Bi, 43.17;	Cl, 32.97
Found:	C, 11.2 ;	H, 2.37;	S,10.15;	Bi, 43.45;	Cl, 32.75
	11.4	2.51	9.90		*32.49
	*11.19	*2.81			
	*11.12	*2.69			

* Analysed by the laboratory of Carl Tiedke

b) Reaction with excess bismuth chloride.

To a solution containing 2.55 grams (0.015 mole) of trimethylsulfonium sulfate in 51 ml. of solution was added 58.9 ml. (0.02 mole) of N bismuth chloride. The precipitate that formed was filtered off and the material did not melt below 260°. Evaporation of the filtrate gave white crystals that melted at 121-3° and that analysed for $Me_3SCl \cdot BiCl_3$.

Anal:	Calculated for $C_3H_9SBiCl_4$:	S, 7.48
	Found:	S, 7.24

2. Trimethylsulfonium chloride was prepared by treating trimethylsulfonium iodide with moist silver oxide and neutralizing the solution of trimethylsulfonium hydroxide with

hydrochloric acid. To prepare 0.1 mole of trimethylsulfonium chloride, 21.5 grams (0.15 mole) of methyl iodide and 9.3 grams (0.15 mole) of methyl sulfide were mixed in a stoppered flask and cooled in an ice bath. The sulfonium iodide crystallized almost immediately. After recrystallization from water, it decomposed between 202° and 219°, depending on the rate of heating.

The silver oxide was prepared by mixing 17 grams (0.1 mole) of silver nitrate with a slight excess of sodium hydroxide (4.5 grams). The supernatant liquid was decanted and the precipitate washed by decantation until neutral. Then the precipitate was added slowly and with stirring to a solution containing 20.5 grams (0.1 mole) of trimethylsulfonium iodide in 150 ml. of water. The precipitate of silver iodide was filtered off and the solution neutralized with hydrochloric acid.

a) Reaction with an equimolar quantity of bismuth chloride.

The solution of trimethylsulfonium chloride just described was treated with 100 ml. (0.1 mole) of 3N bismuth chloride, by allowing the bismuth chloride to drop slowly into the sulfonium chloride solution. The precipitate that formed was filtered off, and the filtrate evaporated. A compound that was identical with the salt obtained from trimethylsulfonium sulfate and bismuth chloride

was obtained. It melted at 245° with ebullition, and produced no depression of the melting point when mixed with the compound mentioned above.

B. Benzylsulfonium compounds

1. Preparation of benzyl sulfide. The sulfide was prepared by the method of Shriner, Struck, and Jorison (62). A solution of sodium sulfide, containing 140 grams (1.8 moles) of the sulfide in 400 ml. of water, was prepared by saturating half of a solution of 140 grams of sodium hydroxide with hydrogen sulfide and then mixing it with the other half. This solution was added slowly to a solution of 464 grams (3.7 moles) of benzyl chloride in 1200 ml. of alcohol. The mixture was stirred on the steam bath for 34 hours and then allowed to cool. Large crystals of the sulfide deposited on cooling. The liquid was filtered off and extracted with ether. The ether layer was then distilled; the aqueous layer rejected. After removal of the ether, the residue was distilled under a vacuum and the solid obtained was pressed dry. It melted at 47°. The large crystals that had formed in the reaction vessel were ground up and thoroughly washed with water before drying, M.P. 45°. Pure benzyl sulfide melts at 49°. Total yield, 244.8 grams of

crude benzyl sulfide. The recrystallization of benzyl sulfide from 70% alcohol was found to be so time-consuming and unnecessary that the sulfide was used without further purification.

2. Tribenzylsulfonium sulfate

a) From benzyl sulfide, benzyl alcohol, and sulfuric acid. The method of Fichter and Sjöstedt (21) was used. To 10.7 grams (0.05 mole) of benzyl sulfide in 150 ml. of glacial acetic acid and 10 ml. of concentrated sulfuric acid was added 5.4 grams (0.05 mole) of benzyl alcohol and the mixture was allowed to stand for two hours at 70° on the water bath. The glacial acetic acid was then distilled off under a vacuum, care being taken not to raise the temperature of the water bath above 80°. The residue in the flask appeared milky. On treatment with water, a precipitate was obtained almost immediately. It was filtered off, extracted with ether to remove unreacted benzyl sulfide, and recrystallized from water containing a little dilute sulfuric acid. The pure product weighed 9 grams and melted at 174°.

Anal: Calculated for $C_{21}H_{22}S_2O_4$: S, 15.92

Found: S, 16.15, 16.17

b) From benzyl sulfide, methyl alcohol, and sulfuric acid. A solution of 13.1 grams (0.06 mole) of benzyl

sulfide in 150 ml. of glacial acetic acid and 10 ml. of concentrated sulfuric acid was reacted with 2.5 ml. (0.06 mole) of absolute methyl alcohol. The mixture was warmed to 70° on the water bath for two hours. After the glacial acetic acid was removed by distillation under a vacuum, the residual liquid consisted of two layers. When an attempt was made to separate these, the upper layer solidified in the separatory funnel and proved to be unreacted benzyl sulfide. The lower layer gave a white precipitate on treatment with water. After extraction of the precipitate with ether, it was recrystallized from water containing dilute sulfuric acid. It melted at 174° and a mixed melting point with the salt obtained in 2 a) showed no depression. Consequently, here also tribenzylsulfonium sulfate was produced.

c) From benzyl sulfide and dimethyl sulfate in glacial acetic acid. The tribenzylsulfonium sulfate was produced, in this case, by dissolving 21.4 grams (0.1 mole) in 200 ml. of glacial acetic acid and adding 6.3 grams (0.05 mole) of dimethyl sulfate. The mixture was heated on the water bath for three hours and then the glacial acetic acid was distilled off under a vacuum. When the residual liquid was poured into water, a crystalline material and an oil were obtained. When the oil had solidified, the solid material was filtered off and after extraction of unreacted

benzyl sulfide with ether, it was recrystallized from water containing dilute sulfuric acid. It melted at 173° (here also the melting point depends upon the rate of heating and Fichter and Sjöstedt (21) give 170°-175°), and caused no lowering of the melting point when mixed with the tribenzylsulfonium sulfate obtained in 2 a).

Anal: Calculated for $C_{21}H_{22}S_2O_4$: S, 15.92

Found: S, 16.03

3. Bis-benzyldimethylsulfonium chloride · bismuth chloride was prepared from a solution of the corresponding sulfonium sulfate on addition of bismuth chloride as follows; a solution of 3.7 grams (0.06 mole) of methyl sulfide in 150 ml. of glacial acetic acid and 10 ml. of concentrated sulfuric acid was reacted with 6.5 grams (0.06 mole) of benzyl alcohol. The mixture was allowed to stand at room temperature for twelve days. The glacial acetic acid was then distilled off and the residue treated with water. An oil formed, so glacial acetic acid was added to redissolve the oily sulfonium sulfate and then bismuth chloride was added until no further precipitate was obtained. The crystals that formed melted over a fairly wide range, about 89° to 130°, but on recrystallization from dilute hydrochloric acid a compound melting at 138° to 140°, depending upon the rate of heating,

was obtained. This material, on analysis, proved to be $2C_7H_7(CH_3)_2SCl \cdot BiCl_3$.

Anal: Calculated for $C_{18}H_{26}S_2BiCl_5$:
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

4. Tris-benzyldimethylsulfonium chloride·bis-bismuth chloride.

This salt was obtained in the following manner. Benzene was used to dissolve 21.4 grams (0.1 mole) of benzyl sulfide and 12.6 grams (0.1 mole) of dimethyl sulfate was added. The mixture was heated on the water bath for 14 hours and then 100 ml. of water was added and the heating continued for another seven-hour period. At the end of that time, the benzene layer was darkish brown, while the aqueous layer was colourless. The two layers were separated and the benzene layer allowed to evaporate. Very large crystals of benzyl sulfide were obtained after some time. The aqueous layer was treated with bismuth chloride by slowly adding it and 100 ml. of 3N bismuth chloride (0.1 mole) simultaneously to 100 ml. of 3N hydrochloric acid. The cloudiness that developed repeatedly was cleared by the addition of a total of 300 ml. of 6N hydrochloric acid. A small amount of gummy precipitate formed, which was discarded. The filtrate, on evaporation gave a white precipitate. This was filtered

off and dried. It could not be recrystallized from dilute hydrochloric acid, so it was extracted with benzene, alcohol, and acetone. It became crystalline during the treatment with acetone, but still could not be recrystallized from dilute hydrochloric acid. It was found to be quite soluble in Carbitol and could be precipitated from this reagent with acetone. The needles that formed, after further purification in the same manner, melted at 140° and decomposed at 145°. Analyses for bismuth and sulfur showed that it was $3C_7H_7(CH_3)_2SCl \cdot 2BiCl_3$ and that no rearrangement had occurred.

Anal: Calculated for $C_{27}H_{39}S_3Bi_2Cl_9$:

S, 8.03; Bi, 34.94

Found: S, 7.98; Bi, 35.2

C. Butylsulfonium compounds

1. Tris-dibutylmethylsulfonium chloride·bis-bismuth chloride.

To a solution containing 29.2 grams (0.2 mole) of butyl sulfide in 150 ml. of glacial acetic acid and 20 ml. of concentrated sulfuric acid was added 4 ml. (0.1 mole) of absolute methyl alcohol. The solution became cloudy and heat was evolved. After warming for an hour on the water bath, the solution had turned a deep reddish brown. It was allowed

to stand for about two and a half months. Then the glacial acetic acid was distilled off under a vacuum. Nothing crystalline could be obtained by treating the reddish-brown residual liquid with water. Since the solution was not clear but contained oily droplets, it was extracted with ether before the treatment with bismuth chloride. Evaporation of the ether gave a reddish-brown oil that was not further investigated.

The clear aqueous solution and 100 ml. (0.1 mole) of 3N bismuth chloride were dropped into 100 ml. of 3N hydrochloric acid. The solution was filtered to remove oily droplets and allowed to stand over night. By the next day, crystals had formed. These were filtered off and found to melt at 150°-152°. After one recrystallization from dilute hydrochloric acid, it melted at 153°-154°, and was probably $2(C_4H_9)_2CH_3SCl \cdot BiCl_3$; but insufficient material was obtained for analyses. The filtrate, on evaporation, gave crystals that melted at 91°. On recrystallization from dilute hydrochloric acid, however, the melting point rose to 163°-165° (ebullition). After another recrystallization the compound melted with ebullition at 164°. Analyses proved that it was $3(C_4H_9)_2CH_3SCl \cdot 2BiCl_3$.

Anal: Calculated for $C_{27}H_{63}S_3Bi_2Cl_9$:
C, 26.56; H, 5.16; S, 7.87
Found: C, 26.62; H, 5.06; S, 7.74

D. Analytical Details

Having had some difficulties in the analyses of these bismuth chloride double salts of sulfonium chlorides, I should like to make the following observations.

1. The sulfur analyses, whether done according to the Parr bomb or the Carius procedure, were among the most reliable. The bismuth evidently does not interfere in any way with the precipitation of the sulfate ion as barium sulfate. When the Parr bomb was used, 2 grams of a 2 : 1 potassium nitrate - sugar mixture was added to a .2 to .3 gram sample to accelerate the combustion. Otherwise, the regular procedures were followed.

2. No difficulties were experienced with the carbon-hydrogen determinations. The only possible difficulty here would arise if the weighing tube were of insufficiently wide bore to permit passage of the combustion products when the bismuth oxide is formed (63)(64).

3. The chloride analysis required removal of the bismuth present. Attempts to remove the bismuth as the hydroxide were unsuccessful, as the precipitation of bismuth hydroxide by ammonium hydroxide is incomplete unless an ex-

cess of ammonium chloride is added (65).

Attempts to remove the bismuth as the carbonate by first treating the acid solution with sodium carbonate, filtering off the bismuth basic carbonate, dissolving it in nitric acid, and reprecipitating it with ammonium carbonate, gave poor results. Almost no precipitate of silver chloride was obtained after acidification of the filtrate, indicating that the greater part of the chloride had precipitated with the bismuth as the oxychloride. Consequently the bismuth values were also incorrect.

The chloride in the trimethylsulfonium compound was determined after removal of the bismuth by fusion of the compound with a potassium nitrate - potassium carbonate mixture. Details of this bismuth determination will be given later. This method, however, could not be used for compounds containing a higher percent of carbon, as the chloride was volatilized at the temperature necessary for the decomposition of the organic matter. Consequently, it was considered sufficient to base the composition of these compounds upon analyses for carbon, hydrogen, sulfur, and bismuth.

4. Bismuth analyses were attempted by numerous methods, only one of which proved to be satisfactory. Precipitation as the oxychloride can be used only for compounds containing not more than 5 milligrams of bismuth per sam-

ple (66). Precipitation as hydrated bismuth oxide with ammonium hydroxide is unsatisfactory as the precipitation can produce the oxychloride, thus giving inaccurate results.

Analyses using Cupferron did not give satisfactory results, although the method given by Prodinger (67) was followed. The method that Blättler (57) used in analysing her double salts was also found to give inaccurate results. Hillebrand and Lundell (66) claim that bismuth cannot be precipitated as the carbonate from solutions containing anions with which the bismuth can form insoluble basic salts. This naturally includes solutions containing chloride, bromide, or sulfate ions.

The only method that was found to give accurate results was the method of de Myttenaere (68), who used it to analyse quinine iodobismuthate. Five hundred milligrams of the substance is mixed with four grams of a potassium nitrate - potassium carbonate (anhydrous) mixture (1 : 2). After mixing with a dry stirring rod, 10 ml. of water is added little by little while stirring. The mixture is heated to dryness on the water bath and then heated cautiously to destroy organic matter. I found that when the cooled melt was orange in color low results for bismuth were obtained. Heating until the cooled product was yellow in color gave accurate results. The benzylsulfonium compounds were heated to between 450° and 500° in a muffle furnace,

whereas the trimethylsulfonium salts could be heated at a lower temperature. When the residue is pure yellow, it is taken up in warm water and washed by decantation through an ash-free filter until the washings are absolutely neutral. The filter is ignited, a few drops of concentrated nitric acid added to oxidize any bismuth reduced by carbon from the filter, heated again, and the bismuth weighed as Bi_2O_3. It was found that the original ignition with the fusion mixture could not be carried out in a porcelain evaporating dish, as the porcelain surface was eroded by the fusion mixture. A platinum evaporating dish can be used satisfactorily.

PART V

SUMMARY

The reaction of organic sulfides with organic sulfates was investigated to determine whether any evidence could be found for a rearrangement similar to those which are known to occur in the formation of sulfonium halides. Such rearrangements were found to occur in three cases: 1) in the reaction of benzyl sulfide with methyl hydrogen sulfate; 2) in the interaction of benzyl sulfide and dimethyl sulfate in benzene; and 3) in the reaction between benzyl sulfide and dimethyl sulfate in glacial acetic acid. In the first case, tribenzylsulfonium sulfate was obtained instead of the dibenzylmethylsulfonium sulfate normally expected; in the second, a double salt of benzyldimethylsulfonium chloride was produced, and no dibenzylmethyl compound was isolated; and in the third case, the tribenzyl compound was also formed instead of the dibenzylmethyl sulfonium salt.

The mechanism proposed for the formation of sulfonium halides by Ray and Levine (5) has been extended to the sulfonium sulfates. The theoretical sulfonium salt is formed temporarily, but dissociates in different ways. The new sulfides and sulfates produced then recombine to form the most stable sulfonium sulfates. The mechanism is most simply illustrated by the following general equations:

$$R_2S + CH_3SO_4H \rightleftharpoons R_2CH_3SSO_4H$$

$$R_2CH_3SSO_4H \rightleftharpoons RSCH_3 + RSO_4H$$

$$R_2S + RSO_4H \rightleftharpoons R_3SSO_4H$$

$$RSCH_3 + CH_3SO_4H \rightleftharpoons R(CH_3)_2SSO_4H$$

The following new compounds were prepared during this investigation:

Compound	Melting Point	Colour and Form
$(CH_3)_3SCl \cdot BiCl_3$	121°	white crystals
$3(CH_3)_3SCl \cdot 2BiCl_3$	245°(dec.)	white, glistening prisms
$2C_7H_7(CH_3)_2SCl \cdot BiCl_3$	140°(dec.)	white plates
$3C_7H_7(CH_3)_2SCl \cdot 2BiCl_3$	145°(dec.)	white needles
$3(C_4H_9)_2CH_3SCl \cdot 2BiCl_3$	164°	flat white plates

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