XVII.—*Action of Alkyl Iodides on the Mercuric Iodide Sulphides of the Fatty Series.*

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SOME years ago, Krüger (*J. pr. Chem.*, 1876, [ii], 14, 207) investigated the action of methyl iodide on methyl ethyl sulphide, and of ethyl iodide on dimethyl sulphide, and found that in each case a different dimethylethylsulphine iodide was produced. This work was repeated by Nasini and Scala (*Gazzetta*, 1888, 18, 67) a few years later and confirmed. Klinger and Maassen (*Annalen*, 1888, 243, 193), however, in a careful series of experiments, obtained by the two methods identical sulphine iodides which gave rise to identical series of double salts. At the same time, they pointed out that Krüger's method of preparation was at fault and that his substances were impure.

From the facts that conflicting results have been obtained, and that the bulk of the evidence in these researches is based upon the behaviour of certain double salts, it seemed possible that an investigation of these substances might throw some light upon the matter. The following research has therefore been undertaken, firstly, to attempt to determine the constitution of the double salts of the sulphine bases, and, secondly, to ascertain whether, by varying the methods of preparation, stereoisomeric compounds could be obtained.

In acetone or alcoholic solution, the sulphides unite with mercuric iodide to form compounds of the general formula R_2SHgI_2 . These are analogous to such substances as R_2SI_2 , R_2SBr_2 , R_2SRI , &c., and their constitution must therefore be represented in a corresponding manner, that is, as containing quadrivalent sulphur:
$$\begin{array}{c} R > S < \begin{array}{l} HgI \\ I \end{array} \end{array}$$

Mercuric iodide and the alkyl iodides might be expected to react in a similar way with the mercaptans forming substances such as $\begin{array}{c} R > S < I \\ H > S < HgI \end{array}$ and $\begin{array}{c} R > S < I \\ H > S < R \end{array}$. These, however, do not appear as products of the reaction, and may be assumed to be unstable com-

pounds, formed at an intermediate stage, and readily splitting off hydrogen iodide as follows:

Regarded from this point of view, the acid nature of the alcohols and mercaptans appears to be dependent on the tendency of oxygen and sulphur to become quadrivalent, and since oxygen shows this tendency to a less degree than sulphur, it follows that the alcohols show weaker acid properties than the mercaptans. That this is the case is illustrated by the fact that ethyl mercaptan, dissolved in an alcoholic solution of sodium ethoxide, shows all the reactions of sodium mercaptan; for example, on treating with alkyl iodides, the sulphides are formed.

The alkyl iodides react with the mercuric iodide compounds of the sulphides to form stable yellow substances, which are found to be identical with those produced from the corresponding sulphine iodides and mercuric iodide. Accordingly, their formation must be represented as follows:

Dobbin and Masson (Trans., 1885, 47, 56) have already investigated the products of addition of the halogens to the sulphine halides, and conclude that they are not molecular compounds, but owe their formation to either sexavalent sulphur or trivalent iodine. From their stability and from the fact that the sulphine sulphates give similar compounds, these authors incline to the former hypothesis.

In support of this view, I have found that dimethyl sulphide bromide, $(\text{CH}_3)_2\text{SBr}_2$, reacts with methyl iodide to give the same substance, $(\text{CH}_3)_3\text{SBr}_2\text{I}$, as is produced from trimethylsulphine iodide and bromine in molecular proportion.

The following series of reactions were carried out with the object of investigating the stereochemical properties of sexavalent sulphur. As yet, only negative evidence has resulted. It has been found that the same compound of trimethylsulphine iodide with mercuric iodide is produced in the following three different ways.

From dimethyl sulphide-mercuric iodide and methyl iodide:

From trimethylsulphine iodide and mercuric iodide:

From dimethyl sulphide iodide and mercury methyl iodide :

The following two reactions also give identical products.

Triethylsulphine iodide and mercuric iodide :

Diethyl sulphide, mercuric iodide, and ethyl iodide :

The same process has been applied to derivatives containing only two of the three alkyl groups alike.

The following reactions give identical products.

Dimethylethylsulphine iodide and mercuric iodide :

Methyl ethyl sulphide-mercuric iodide and methyl iodide :

Dimethyl sulphide-mercuric iodide and ethyl iodide :

Also the same compound of diethylmethylsulphine iodide with mercuric iodide is produced by the following reactions.

Diethylmethylsulphine iodide and mercuric iodide :

Diethyl sulphide-mercuric iodide and methyl iodide :

Methyl ethyl sulphide-mercuric iodide and ethyl iodide :

From these results, no definite conclusion can be drawn as to the relative directions of the six valencies of sulphur. Even the simplest arrangement, that in which the valencies are directed towards the six angles of an octahedron, allows of three possible isomerides in the case of $(\text{CH}_3)_3\text{SIHgI}_2$. Where the alkyl groups differ, the possible number becomes still larger. As, however, Wedekind (*Ber.*, 1899, 32, 517) and others have shown that quaternary ammonium compounds containing two or more small groups, such as methyl and ethyl, are not obtained in isomeric forms, and that the presence of more complex groups, as phenyl or benzyl, renders this isomerism possible, it is desirable to repeat these experiments with derivatives containing larger radicles.

It is a noteworthy feature of these reactions that the presence of mercuric iodide appears to render the addition of alkyl iodide far easier of accomplishment than is the case in its absence. Thus, for example, the action of ethyl iodide on dimethyl sulphide-mercuric iodide is complete in 10 to 15 minutes with the formation of $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{SIHgI}_2$, whilst, on the other hand, the production of dimethylethylsulphine iodide from ethyl iodide and dimethyl sulphide is scarcely complete in 3 days.

It is hoped, therefore, that this method of preparation will be of use in obtaining sulphines containing higher radicles and possibly those of the aromatic series, which do not appear to be readily formed by the ordinary methods.

EXPERIMENTAL.

Action of Mercuric Iodide on Alkyl Sulphides.

The sulphides of the fatty series dissolve mercuric iodide with slight evolution of heat and formation of the mercuric iodide-sulphides. These substances are best prepared by shaking up a warm concentrated solution of the sulphide in acetone with mercuric iodide, which dissolves, the solution acquiring a yellow colour. After filtering or decanting from excess of mercuric iodide, the solution is either left to crystallise or, if the product is very soluble, evaporated in a vacuum. These substances are yellow, unstable compounds, the lower members of the series crystallising well in long prisms. They are soluble in acetone, but only sparingly so in alcohol or ether. When exposed to the air or gently warmed, they are decomposed, leaving a residue of mercuric iodide, the same decomposition occurring when they are boiled with water or acids. Potassium hydroxide solution converts them to yellow substances, from which acids regenerate the original mercuric iodide sulphides. On account of their tendency to decompose, and the consequent difficulty in obtaining them sufficiently pure for analysis, their composition was determined as follows. A weighed quantity of

sulphide dissolved in acetone or ether was shaken with a known amount of mercuric iodide in excess. The remaining mercuric iodide was removed by filtration, washed with ether, and, after drying, weighed. Owing to the slight solubility of mercuric iodide in acetone or ether, the numbers obtained were generally a little low.

Dimethyl sulphide-mercuric iodide, $(\text{CH}_3)_2\text{SHgI}_2$, crystallises from acetone in long, yellow needles and melts at 75° . Estimation of the amount of mercuric iodide which entered into combination with the sulphide gave the following results :

0.183 requires 1.322 HgI_2 . $\text{HgI}_2 = 87.8$.

0.235 ,, 1.70 HgI_2 . $\text{HgI}_2 = 87.8$.

$\text{C}_2\text{H}_6\text{I}_2\text{SHg}$ requires $\text{HgI}_2 = 87.9$ per cent.

Methyl ethyl sulphide-mercuric iodide, $\text{CH}_3(\text{C}_2\text{H}_5)\text{SHgI}_2$, crystallises from acetone in pale yellow prisms and melts at 59° . On analysis, the following result was obtained :

0.356 requires 2.166 HgI_2 . $\text{HgI}_2 = 85.9$.

$\text{C}_3\text{H}_8\text{I}_2\text{SHg}$ requires $\text{HgI}_2 = 85.6$ per cent.

Diethyl sulphide-mercuric iodide, $(\text{C}_2\text{H}_5)_2\text{SHgI}_2$, crystallises from acetone, in which it is very soluble, in pale yellow prisms and melts at 52° . It was analysed by weighing the residue of mercuric iodide obtained by gently heating a known quantity to a temperature slightly above its melting point.

0.3026 gave 0.2516 HgI_2 . $\text{HgI}_2 = 83.14$.

0.5505 ,, 0.4565 HgI_2 . $\text{HgI}_2 = 82.92$.

$\text{C}_4\text{H}_{10}\text{I}_2\text{SHg}$ requires $\text{HgI}_2 = 83.45$ per cent.

Amyl sulphide-mercuric iodide, $(\text{C}_5\text{H}_{11})_2\text{SHgI}_2$, is obtained as a yellow oil which easily decomposes on heating. On analysis, it gave the following result :

0.5 requires 1.24 HgI_2 . $\text{HgI}_2 = 71.2$.

$\text{C}_{10}\text{H}_{22}\text{I}_2\text{SHg}$ requires $\text{HgI}_2 = 72.2$ per cent.

Dibenzyl sulphide-mercuric iodide, $(\text{C}_7\text{H}_7)_2\text{SHgI}_2$, is very soluble in acetone ; it crystallises in pale yellow, transparent plates and melts at $37-38^\circ$. It is exceedingly unstable in the solid state and decomposes on being pulverised, but is more stable when in solution. On analysis, the following numbers were obtained.

1.1435 requires 2.53 HgI_2 . $\text{HgI}_2 = 68.8$.

0.926 ,, 2.05 HgI_2 . $\text{HgI}_2 = 69.0$.

$\text{C}_{14}\text{H}_{14}\text{I}_2\text{SHg}$ requires $\text{HgI}_2 = 67.9$ per cent.

Of the foregoing derivatives, some are stated to have already been obtained. Loir (*Annalen*, 1858, 107, 234) claims to have prepared the dimethyl (m. p. 67°) and the diethyl derivative (m. p. 110°) by the

action of ethyl iodide on dimethyl sulphide-mercuric chloride and diethyl sulphide-mercuric chloride respectively, and describes them as stable yellow substances. These are evidently derivatives of sulphine bases, since, as shown below, such substances are produced from alkyl iodides and the mercuric iodide sulphides.

Compounds of Sulphine Iodides with Mercuric Iodide. Action of Alkyl Iodides on the Mercuric Iodide Sulphides.

The alkyl iodides dissolve the mercuric iodide sulphides, and on allowing the solutions to stand for a few minutes they become warm, gradually acquiring a bright yellow colour. Precipitation with ether yields yellow, crystalline products, identical with those produced from the corresponding sulphine iodides and mercuric iodide. These are stable, yellow, crystalline substances, and, especially in the case of the lower members of the series, can be easily obtained in large, well-defined crystals. They show a slight tendency to split off mercuric iodide, although to a far less degree than the mercuric iodide sulphides. When suspended in water in the finely divided state and boiled, only a very slight decomposition occurs. With potassium hydroxide solution, they yield a white substance soluble in acetone.

The mercury in these compounds was estimated as follows. The substance was decomposed by treatment with nitric and hydrochloric acids, and the solution evaporated to dryness. The resulting mercuric chloride was dissolved in water, and from the solution, after neutralising with sodium carbonate and then acidifying with hydrochloric acid, the mercury was precipitated as sulphide and estimated in the usual manner.

It may be noted that all the following reactions appear to take place quantitatively.

Trimethylsulphine iodide-mercuric iodide, $(\text{CH}_3)_3\text{SIHgI}_2$, was prepared in three ways.

1. The calculated quantities of trimethylsulphine iodide and mercuric iodide were shaken up with acetone. From the yellow solution, ether precipitated a crystalline substance melting at 163° , which, after recrystallisation from acetone, melted at 165° . By allowing a cold solution in acetone to evaporate spontaneously, it was deposited in large, yellow prisms often half a centimetre across.

2. Dimethyl sulphide-mercuric iodide was dissolved in an excess of methyl iodide; interaction took place with slight evolution of heat, and was complete in two minutes. On cooling, a substance separated out which melted at 163 – 164° , and from the mother liquor a further quantity was obtained by precipitation with ether. After precipitating twice from acetone with ether, it melted at 165° .

3. The substance was also produced from dimethyl sulphide

iodide and mercury methyl iodide, but whether the reaction may be regarded as an additive one is a matter of doubt. 0.6 gram of dimethyl sulphide and 2.5 grams of iodine were dissolved in 5 c.c. of acetone and 3.4 grams of mercury methyl iodide added. In about 15 minutes, the reaction was complete, and on cooling the mixture in ice a crystalline precipitate was obtained melting at 140—145°.

After precipitating twice from acetone with ether and crystallising once from acetone, it melted at 163—164°. Together with this substance there was formed another, which may be obtained from the mother liquor; it melted at 68—70°, and on analysis showed rather a high percentage of mercury (31.05 per cent.). Analyses of the substances prepared by the above three methods were made, with the following results:

I.	0.3686	gave	0.1289 HgS.	Hg = 30.17.
II.	0.3513	„	0.1235 HgS.	Hg = 30.29.
III.	0.2129	„	0.0755 HgS.	Hg = 30.56.
	0.2410	„	0.0855 HgS.	Hg = 30.58.
$C_3H_9I_3SHg$ requires Hg = 30.39 per cent.				

It is evident from these results that the substance obtained by the third method still contained a small quantity of the compound of lower melting point.

Triethylsulphine iodide-mercuric iodide, $(C_2H_5)_3SIHgI_2$, was obtained by two methods. It was found that concentrated acetone solution of trimethylsulphine iodide, when saturated with mercuric iodide and precipitated with ether, formed a yellow, crystalline substance which melted at 116°, and on analysis the following result was obtained:

0.5372	gave	0.2143 HgS.	Hg = 34.38.
$(C_2H_5)_3SI, 2HgI_2$ requires Hg = 34.66 per cent.			

1. The following method was therefore used for the preparation of the required compound. An acetone solution of triethylsulphine iodide was divided into two equal parts, one of which was shaken with excess of mercuric iodide. After filtering, the solution was added to the second part and the whole concentrated by spontaneous evaporation. By precipitation with ether, a substance was obtained which melted at 107—108°, and after purification crystallised in bright yellow leaflets melting at 112°.

2. Diethyl sulphide-mercuric iodide was dissolved in excess of ethyl iodide and the interaction, which took place with evolution of heat, was complete in about fifteen minutes. On the addition of ether, a substance was precipitated which melted at 109—110° and after recrystallisation at 112°.

Analyses of the products of the above reactions were made, with the following results :

- I. 0.2462 gave 0.0810 HgS. Hg = 28.35.
 II. 0.2593 „ 0.0857 HgS. Hg = 28.48.
 $C_6H_{15}I_3SHg$ requires Hg = 28.57 per cent.

Dimethylethylsulphine iodide-mercuric iodide, $(CH_3)_2(C_2H_5)SIHgI_2$, was prepared by three methods.

1. Dimethylethylsulphine iodide was dissolved in acetone and the calculated quantity of mercuric iodide added. From the solution, ether precipitated a substance which melted at 85° and, when pure, crystallised from acetone in long, yellow prisms melting at 87° .

2. Dimethyl sulphide-mercuric iodide was dissolved in excess of ethyl iodide, and after standing for 12 to 15 minutes, the interaction was complete. From the solution, a yellow, crystalline substance melting at 85° was precipitated by ether, and this, when recrystallised from acetone, formed long prisms which melted at 86.5° .

3. An excess of methyl iodide was added to methyl ethyl sulphide-mercuric iodide, and the interaction, which took place immediately with slight evolution of heat, was complete in about 2 minutes. On adding ether, a yellow substance melting at $78-79^\circ$ was obtained, which, after reprecipitating twice from acetone, melted at 87° .

When the mixture of methyl iodide and methyl ethyl sulphide-mercuric iodide was allowed to stand longer than about 15 minutes, an impure product was obtained. In one experiment, the mixture was allowed to stand for 2 hours, and a crystalline substance was then obtained which melted at $160-161^\circ$, and was evidently the trimethyl derivative. The solution contained a mixture of other substances.

Analyses of the products of the above three reactions were made, with the following results :

- I. 0.43 gave 0.1483 HgS. Hg = 29.72.
 II. 0.5981 „ 0.2050 HgS. Hg = 29.54.
 III. 0.4512 „ 0.1545 HgS. Hg = 29.51.
 $C_4H_{11}I_3SHg$ requires Hg = 29.76 per cent.

Methyldiethylsulphine iodide-mercuric iodide, $CH_3(C_2H_5)_2SIHgI_2$, was also obtained in three ways.

1. 2.5 grams of methyldiethylsulphine iodide were dissolved in acetone and 4.9 grams of mercuric iodide added. From the solution, ether precipitated a yellow, crystalline substance which melted at $64-65^\circ$, and after reprecipitating twice from acetone by ether, at 67° ; its acetone solution, when allowed to evaporate spontaneously, deposited large, transparent, yellow plates.

2. A concentrated solution of 6 grams of diethyl sulphide mercuric

iodide was treated with an excess (3 grams) of methyl iodide. After standing for 3 minutes, the solution was precipitated with ether, giving 5 grams of a yellow, crystalline compound melting at 63—64°. After purification, the product melted at 67°, and could be easily obtained in large plates.

3. Methyl ethyl sulphide-mercuric iodide was dissolved in ethyl iodide, and in a quarter of an hour the reaction was complete. The product obtained by precipitation melted at 60—62°, but when purified by solution in acetone and precipitation with ether, at 66·5°.

When the substances prepared by these methods were analysed, the following numbers were obtained :

- I. 0·6543 gave 0·2213 HgS. Hg = 29·15.
 II. 0·3950 „ 0·1330 HgS. Hg = 29·02.
 III. 0·3051 „ 0·1027 HgS. Hg = 29·01.
 $C_5H_{13}I_3SHg$ requires Hg = 29·15 per cent.

It appears, then, so far as these experiments go, that no isomerism exists among the compounds which the sulphine iodides form with mercuric iodide. Although the supposition that these substances contain sexavalent sulphur allows of its possibility, isomerism does not follow as a necessary consequence, for, as already pointed out in the introduction, similar isomerism among the nitrogen compounds is non-existent in the lower members of the series, and only appears when the nitrogen is united to larger and more complex radicles.

In connection with this work, attempts have been made to resolve methyl ethyl thetine, $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > S < \begin{matrix} CH_2 \cdot CO \\ O \end{matrix}$, into optically active components, but without success. It was found that any attempts to prepare a strychnine or cinchonine salt of the hydrobromide of the thetine, $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > S < \begin{matrix} CH_2 \cdot CO_2H \\ Br \end{matrix}$, resulted in the formation of its anhydride and the hydrobromide of the active base. Silver malate and the thetine hydrobromide gave similar results. Experiments were also made with *Penicillium glaucum*, but it was found that only a very slight growth of the mould took place after standing for some weeks with a 2 per cent. solution of the anhydride, the solution being inactive.

In conclusion, I wish to express my thanks to Professor Ramsay for the interest he has taken in the work described in this paper, and the help he has afforded me in carrying it out.

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