

LXV.—*Metallic Compounds containing Bivalent Hydrocarbon Radicles.* Part II.

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IN a former communication (*Chem. Soc. J.*, 1880, Trans., 658) an account was given of a new organo-mercury compound, of which the interesting feature was the bivalent character of the hydrocarbon radicle contained in it, viz., methylene; this being, so far as I can ascertain, the first body ever obtained of its class. The bivalent function of the organic radicle, as well as of the metal, naturally suggests the existence of a second compound similar to the first, but containing an additional atom of mercury. Thus—

- (1.)  $\text{I}(\text{CH}_2)\text{HgI}$ .
- (2.)  $\text{IHg}(\text{CH}_2)\text{HgI}$ .

This second compound, which is related to methylene iodide in the same way as mercuric iodomethide,  $(\text{CH}_3\text{HgI})$ , is to methyl iodide,

can be easily obtained by exposing a mixture of methylene iodide with an excess of mercury to the action of light. It is desirable to add a little mercuric iodide, so as to form mercurous iodide, which keeps the metal in a finely divided state, and facilitates the reaction. Mercurous iodide also acts chemically by liberating mercury and reproducing mercuric iodide, as explained in the paper already referred to.

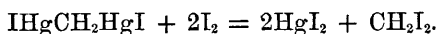
On a bright sunny day the reaction shows itself abundantly in a few minutes, and the mixture gets so thick that it becomes necessary to add some liquid so as to render it sufficiently fluid. Ether is most convenient for this purpose. The reaction may be carried on either in a sealed tube or in a well-corked bottle, which must be constantly shaken so as to expose as much fresh surface as possible to the action of light. The reaction takes from one to several days, according to the state of the weather and the frequency of shaking. If the mixture has been left for a sufficient length of time with constant shaking, the whole of the methylene iodide will be converted into the di-mercury compound; if not, a small quantity of mono-mercury methylene iodide will generally be found unconverted.

In order to get the di-mercury methylene iodide in a state of purity, the following plan was adopted:—

The tube or the bottle is opened, and its contents transferred to a flask. The ether is distilled off, and the residue is well digested with a strong solution of potassic iodide, which dissolves out mercuric iodide, and decomposes any of the mercurous iodide. It is first washed with an aqueous solution of potassic iodide and then with water, till it is free from mercuric iodide and potassic iodide, and afterwards dried. In order to purify it from mercury and mono-mercury compound, the whole is dissolved in hot methylene iodide, whereupon any excess of the metal collects at the bottom of the flask or beaker into a globule. The clear liquid is either decanted or passed through a hot filter. Crystals are rapidly deposited on cooling, the first portions consisting of pure di-mercury compound, whilst later crops and the mother-liquor contain the mono-mercury compound. The first crops are drained, washed with methylene iodide, and then thoroughly with ether, till a drop of the washing rapidly evaporates without leaving any oily residue.

Di-mercury methylene iodide thus obtained is a yellowish crystalline powder, insoluble in all the ordinary solvents, soluble only in hot methylene iodide. Even in that liquid it dissolves to a much less extent than the mono-mercury compound, and only on heating. It melts somewhere about 230° C. with partial decomposition. The method employed for ascertaining its composition is exactly the same as that described in the previous paper, viz., heating it in a sealed tube with a known quantity of pure iodine, ascertaining how much iodine has

been taken up, and determining the quantity of mercury obtained from it. Mercuric iodide and methylene iodide were, as before, the only products of the reaction—



Analytical results are shown below:—

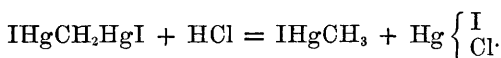
	I.	II.
Substance taken .....	0·58000	0·4230
Pure iodine taken .....	0·55600	0·4731
„ „ left .....	0·11592	0·1513
„ „ used up .....	0·44008	0·3218
Also mercuric sulphide ....	0·40600	0·2939

These data give the following numbers per cent.:—

	I.	II.	Calc. for $\text{CH}_2\text{Hg}_2\text{I}_2$ .
Iodine used up .....	75·88	76·08	76·05
Mercury .....	60·34	59·91	59·88

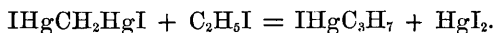
The same compound may also be obtained from the mono-mercury compound,  $(\text{CH}_2\text{HgI}_2)$ , by simply mixing the latter with some mercury, and exposing the mixture to the action of light. It is desirable, as before, to add some mercuric iodide and ether, and the tube or the bottle must be frequently shaken. The product is purified in exactly the same manner as before.

On heating di-mercury methylene iodide with an aqueous solution of potassic iodide or with dilute hydrochloric acid, it yields mercuric iodomethide, which may be sublimed up along the neck of the flask—



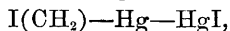
The same product seems also to be formed by heating the compound with ethyl bromide or iodide to about  $140^\circ$  in a sealed tube. When ethyl bromide or iodide which has been so treated, is shaken up with a strong solution of potassic iodide, and gently distilled over a water-bath, some crystalline product is left behind, soluble in ether, alcohol, ethyl bromide, or ethyl iodide, and crystallisable therefrom in thin shining plates, which have the characteristic odour of mercuric iodomethide or iodoethide, and melt at  $143^\circ$ , corresponding therefore with the melting point of the former of these compounds.

How that body is formed is difficult to understand. What had been expected to be formed was mercuric iodo-propide, thus—



The investigation is still being continued in this direction, with the view of building up propyl-compounds from those of ethyl.

In the previous communication it was stated that a body insoluble even in hot methylene iodide is formed, together with mono-mercury methylene iodide, and that this body was supposed to be  $\text{CH}_2\text{Hg}_2\text{I}_2$ . The existence of a body having that formula, and *soluble* in hot methylene iodide being fully established by the experiments above described, a question arose as to what this insoluble body could be. That it may be an isomeride, having the constitution—



was highly improbable, on account of its great stability, even boiling hydric chloride failing to separate metallic mercury from it. Pains were therefore taken to get the body in as pure a condition as possible, and on a careful examination it was found that the product formed by the action of iodine upon it was not methylene iodide, but iodoform. The numerical results of the analysis remained, however, nearly the same as before, *i.e.*, as for  $\text{CH}_2\text{Hg}_2\text{I}_2$ . This is exactly what it ought to be, if the insoluble body has the formula  $\text{CHHg}_3\text{I}_3$ —a new organo-mercury compound, containing a trivalent radicle, and related to iodoform in the same way as iodomethide of mercury is to methyl iodide, or di-mercury methylene iodide to methylene iodide.

The numbers experimentally obtained, and those calculated for  $\text{CHHg}_3\text{I}_3$  and  $\text{CH}_2\text{Hg}_2\text{I}_2$ , differ so little from one another, as shown below, that the former statement with regard to the nature of the insoluble compound, put with caution, may be regarded as not without foundation.

	Experiments.		$\text{CHHg}_3\text{I}_3$ .	$\text{CHHg}_2\text{I}_2$ .
	I.	II.		
Iodine used up . . . . .	75·72	76·01	76·66	76·05
Mercury . . . . .	60·79	60·84	60·36	59·88

The formation of this compound is probably due to the presence of iodoform in the original methylene iodide: for that portion of it which was once used in the preparation of mono-mercury methylene iodide does not give any of the insoluble compound with mercury and mercuric iodide. Moreover, when mercury and iodoform are left together in presence of alcohol and exposed to sunlight, there is formed, among others, a yellowish product, which is insoluble in all the ordinary solvents, hot methylene iodide included—and when treated with iodine (after iodoform has been carefully removed) gives iodoform. We may therefore pretty safely conclude that the insoluble body is a compound of iodoform with mercury, and that we now possess the following series of organo-mercury compounds:—

- With methyl iodide. . . . .  $\text{CH}_3(\text{HgI})$ .  
 „ methylene iodide ..  $\text{CH}_2(\text{HgI})_2$  and  $\text{CH}_2(\text{HgI})\text{I}$ .  
 „ iodoform. . . . .  $\text{CH}(\text{HgI})_3$ .

Since the first part of this paper was written, some more reactions have been tried with mono-mercury methylene iodide, ( $\text{CH}_2\text{HgI}_2$ ), which, though of an unintelligible nature at present, are recorded below.

Strong ammonia, potash, or soda turns this compound grey or almost black, with evolution of heat and separation of metallic mercury. A large quantity of ammoniac, potassic, or sodic iodide is formed at the same time. Heated with an aqueous solution of potassic iodide or hydric chloride, it yields mercuric iodomethide; also a brownish insoluble substance, which leaves a black residue on gentle heating.

I wish to record my best thanks to Dr. Williamson for his able assistance, and to Mr. Berry for some of the preparations and analyses.

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