XIII.—*Researches on the Action of the Copper-zinc Couple on Organic Bodies.* Part IX. *Preparation of Zinc-Methyl.*

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In a previous communication (*Chem. Soc. J.*, 1873, page 682) we stated that methyl iodide is but slightly acted upon by the copper-zinc couple, at its boiling point; indeed, so slightly that we did not look upon this as a practical method of preparing the zinc-compound. But from theoretical considerations relative to the formation of the C_nH_{2n+2} hydrocarbons, we arrived at the opinion that this iodide would be slowly acted upon by the zinc of the couple, even at the ordinary temperature.

An examination of this forecast was made by taking a number of dry couples prepared from half a meter of foil as described in this Journal 1877, i, 567, pouring on them 5 c.c. (11 grams) of methyl iodide, well corking the flasks containing the materials, and making daily observations of any changes. In a day or two some white grains were noticeable intermingled with the couple, and adhering to the sides of the vessels, after which no further change could be detected for some time, when it was observed that the liquid was somewhat yellow, and had diminished in quantity. This apparent absorption of liquid continued, and almost as soon as it appeared complete, crystalline plates were seen studding the surface of the uppermost points of the couples, which went on increasing until the whole appeared one uniform beautifully crystalline mass. The times varied for the first and second parts of this reaction, and the whole particulars are set out in the following table:—

Experiment.	Mean temperature.	First signs of crystallisation.	Completion of action.
I.	18° C.	34 days	36 days
II.	"	29 "	31 "
III.	"	43 "	45 "
IV.	"	32 "	36 "
V.	20° C.	37 "	39 "
VI.	"	39 "	43 "
VII.	22° C.	28 "	30 "
VIII.	"	29 "	30 "

Zinc Methiodide.

On removing the corks of the flasks, a slight outrush of gas took place, followed immediately by white fumes within the vessels. The gas which escaped burnt when ignited, with a bluish flame, and it doubtless consisted of zinc-methyl, saturating the nitrogen of the air originally present. From the mode of formation of the crystalline body, and the absence of liquid or gaseous products, it can scarcely be other than the methyl analogue of Frankland's zinc ethiodide; and, from analogy, it might be expected to split up by heat into zinc iodide and zinc-methyl, zinc iodide, zinc, and di-methyl, or into a mixture of these several substances.

A cork with two tubes was fitted into one of the flasks containing the crystalline product from 5 c.c. of the iodide; one of the tubes was connected with a dry hydrogen supply; the other with a condenser with a fitted and weighed receiver. The gas, on passing through the apparatus for a few minutes, was found to be burning with a bluish flame, indicating the presence of zinc. The current of hydrogen was now stopped, and the flask slowly heated from the melting point of the paraffin bath to 100°C . At about 60° a perfectly clear and colourless liquid began to distil; in 15 minutes it ceased. The distillate weighed 2.7 grams. It was very mobile, had a powerful odour, was free from iodine, and very spontaneously inflammable; in fact, had all the properties ascribed by Frankland to zinc-methyl. The residue in the flask was nearly white, and consisted of zinc iodide. The 2.7 grams corresponds with 72 per cent. of the theoretical quantity, which, when we remember that it is less by that which necessarily adhered to the tubule of the condenser, &c., represents pretty closely the possible yield.

Progress of the Action.

Information as to the rate at which this chemical change takes place appeared very desirable. It was obtained by pouring 5 c.c. of the methyl iodide (at the summer temperature) on to each of five couples made as much alike as we could make them, and estimating the action by distilling the zinc-methyl from the product at the end of the first week in one, at the end of the second week in another, and so on. The results are tabulated below:—

Time.	$(\text{CH}_3)_2\text{Zn}$.
7 days	1.387 grams.
14 "	2.063 "
21 "	2.344 "
28 "	2.73 "
31 "	3.72 "

Signs of crystallisation were noticeable only in the last of these couples, and that on the twenty-ninth day. It appears therefore that, although the action probably starts with comparative energy, the methiodide crystallises and perhaps forms only when the whole of the methylic iodide has disappeared. The methiodide is, in fact, very soluble in methylic iodide.

Effect of Temperature and Time.

As already stated, the couple, when boiled with methyl iodide, decomposes it but slowly; but to obtain definite knowledge on this point, we boiled 5 c.c. of the iodide with the usual quantity of couple for 6 hours, and in another experiment for 22 hours. In the 6 hours the equivalent of 0.945 gram of zinc methyl formed, and in the 22 hours 1.4 grams.

The augmented temperature, as was to be expected, expedites the action, but it may be observed that at this higher temperature, as well as at the lower one, the formation of zinc-methiodide takes place in a rapidly-diminishing ratio with regard to time, even when all allowance is made for the diminishing amounts of liquid and zinc. Experiments were made on this point.

Effect of Quantity of Couple.

5 c.c. of the iodide were added at the ordinary temperature to twice the usual quantity of couple, when the action was found to be complete in three days; and when three times the quantity of couple was used and the same quantity of iodide, the action was over in one day; from which it would appear that the time required to bring about the decomposition of a given quantity of this iodide becomes 12 times less by doubling the amount of couple, and 36 times less by trebling it. We can only therefore attribute the rapidly-decreasing action as time advances to the interference of the zinc methiodide.

To study still more completely the changes involved, and in fact to analyse the crystalline body, the following experiment was made:—A flask containing the methiodide from 11.2 grams of methyl iodide, and the apparatus to which it was connected, were freed from air by dry carbonic anhydride, and the methiodide was decomposed in a current of this gas by heating up to 100°C. The zinc-methyl, as it was set free, was passed into dilute sulphuric acid, and the zinc therein was estimated as oxide. It weighed 2.934 grams, equivalent to 3.44 grams of zinc-methyl. The gas resulting from the decomposition of the volatile zinc-compound was collected over a solution of caustic potash. It measured 1,677 c.c. (corrected), and burnt with a somewhat luminous flame, at the same time depositing a small quantity of a yellowish-red substance. After

standing, however, over water for a day, it burnt with an almost colourless flame without the separation of any solid body, and from the quantity collected, and from what is known of the decomposition-products of zinc-methyl by water, there can be no doubt that it was pure, or nearly pure, marsh-gas. Now the 11·2 grams of methyl iodide could yield theoretically 3·75 grams of zinc-methyl, which, in presence of water, would give 1,764 c.c. of marsh-gas and 3·198 grams of zinc oxide, numbers which but very slightly exceed our experimental ones.

It appears then from this inquiry, that the action of our couple on iodide of methyl at the ordinary temperature is to build up zinc methiodide only;* whether in one stage, thus:—

or in two:—

is open to conjecture; and that this methiodide splits up very readily by heat, without fusing, into zinc iodide and zinc methyl, thus:—

The methiodide is also decomposed by light, the white lustrous crystals becoming dark grey or black, probably from the separation of metallic zinc.

On starting this work, we placed 5 c.c. of methyl iodide in contact with the same quantity of zinc foil as has been employed for the couples used in these experiments. The surface of the metal became tarnished, but no signs of the methiodide appeared; and on opening the flask more than seven months afterwards, only a doubtful trace of any zinc-compound was found.

This investigation specially illustrates the value of our couple in bringing about, at a low temperature, a chemical change which can be brought about by its more positive element, only at such a temperature and under such conditions, as occasion the formation of secondary products. It has also furnished a perfect and really simple method of preparing Frankland's most valuable reagent, zinc-methyl: for in the last experiment described the yield of this substance amounts to 91·7 per cent. of the possible quantity, and in another, the results of which are given on the last line of page 108, to 99·2 per cent.

* In two instances out of about 30, the thin closed flasks containing the couple and iodide burst before the action was complete, which we are disposed to attribute to the accidental presence of moisture, giving rise to marsh-gas. All chance of bursting may be prevented by employing a Bunsen valve.