VIII.—*Researches on the Action of the Copper-zinc Couple on Organic Bodies. Part IV. On Iodide of Allyl.*

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AFTER investigating the action of our copper-zinc couple on the iodides of propyl, we turned aside from the series containing the C_nH_{2n+1} radicals, in order to examine its action on the corresponding member of the series which contains the C_nH_{2n-1} radicals.

Action of the Dry Couple on Allyl Iodide.

On pouring the liquid iodide of allyl upon the metallic couple, there is a sensible rise of temperature, but the action, whatever it may be, stops quickly, unless extraneous heat be applied. At 100° the decomposition is moderately rapid, little or no gas is evolved, and the only organic products appear to be a liquid which has the properties of di-allyl, and a non-volatile resin, apparently isomeric with allylene.

In one experiment a flask containing 5 c.c. (9 grams) of the iodide, with the usual amount of the copper-zinc couple (see *Journ. Chem. Soc.*, 1873, p. 969) was heated in a bath of boiling water for two hours. During this time there distilled over a slightly coloured liquid, which weighed 2.6 grams. On re-distilling this liquid, the first portion that came over, about one-third of the whole, was colourless, mobile, lighter than water, and capable of combining with sulphuric acid to form a brown, treacly mass. The remaining two-thirds consisted principally of undecomposed allyl iodide. Neither of these portions contained a trace of zinc. The flask was then heated to 200° for half-an-hour, but no further allyl iodide, or any other volatile body, was driven off, and the residue was treated with water. This

issolved out the iodide of zinc, but left a resinous body, which was insoluble in alcohol, but readily soluble in ether. Its ethereal solution, on evaporation, gave a brownish substance, which, when dried at 100°, weighed 0.31 gram. An ultimate analysis was made of 0.2060 gram., which yielded 0.6805 CO₂ and 0.181 H₂O. This indicates it to be a hydrocarbon, and probably of the composition $n(C_3H_4)$, the slight excess of carbon being probably due to some carbonization having taken place during the drying of the body, as was rendered the more likely by its somewhat brown colour.

	Calculated, C ₃ H ₄ .	Found.
Carbon.....	90.00	90.10
Hydrogen.....	10.00	9.76
	<hr/> 100.00	<hr/> 99.86

The iodide of zinc formed in this experiment was determined, and it showed that 6.8 grams of the iodide had been decomposed; and the quantities of the two organic products lead to the conclusion that the major part was split up by the action of the couple into iodide of zinc and diallyl, thus:—

while about a fifth part was in some way deprived of hydrogen, but instead of forming gaseous allylene, C₃H₄, it formed apparently an isomeric or polymeric modification. If this C₃H₄ were due to the splitting up of diallyl, $\left\{ \begin{array}{l} C_3H_5 \\ C_3H_5 \end{array} \right.$, its complementary hydrocarbon would of course be produced, as in the case of the C_nH_{2n+1} series; but this was never the case, and we are disposed to attribute the reduction of oxide of zinc unavoidably present in the couple, especially as a trace of water was always observed during the reaction.

Unwilling to relinquish the hope of obtaining zinc-allyl, we tried the action of the couple on the iodide in presence of ether. A decomposition was found to take place at the ordinary temperature, and to proceed rapidly. In one experiment, where 9 grams of the iodide were mixed with twice its volume of pure ether at 12°, the temperature immediately rose; the flask was immersed in water at 12° for 15 minutes, and on removing it, the temperature again rose, but in 10 minutes it had cooled. Little or no gas was evolved, and the products of the reaction were entirely in solution. An estimation of the iodine in combination with zinc showed that 8.43 grams of the iodide, or nearly the whole quantity, had been decomposed. Now if the reaction under these circumstances were simply $2C_3H_5I + Zn = ZnI_2 + \left\{ \begin{array}{l} C_3H_5 \\ C_3H_5 \end{array} \right.$, the

atomic ratio of the iodine to the zinc in the solution would be 1 : 0·5; but if a reaction should take place similar to that which occurs with the monad positive radicals of the alcohol series, viz., $C_3H_5I + Zn = ZnC_3H_5I$, then it is evident that the atomic ratio of the iodine to the zinc would be 1 : 1. In the experiment detailed above the ratio was found to be 1 : 0·587. Thinking that this excess of zinc might arise from the presence of some alcohol or water in the ether employed, though it had been distilled three times from sodium, a portion of the same ether was boiled with sodium for $2\frac{1}{2}$ hours, and then carefully distilled from the same metal. To obviate any injurious rise of temperature on mixing the materials, the flask was kept immersed in water at 11° , and it was suffered to remain untouched for two hours. The reaction was complete. The ethereal solution, on shaking with water, gave a precipitate of zinc oxide, and the ratio of the iodine and zinc was found to be 1 : 0·584, the same as in the previous experiment. On another trial, in which the temperature was kept still lower, and the decomposition not allowed to proceed to completion, the ratio was found to be 1 : 0·600.

This excess of zinc can scarcely therefore be attributed to the presence of any alcohol or water in the ether employed. Moreover, had it been so, there would have been found, as will be presently shown, about 120 c.c. of propylene. No gas, however, was evolved. Yet this is inconclusive, for ether itself is capable of dissolving propylene, indeed we found it to dissolve 12·8 times its volume at 13° , and therefore the gas would scarcely make its appearance as such. But this objection is susceptible of an answer, for a mixture of alcohol and water, just capable of dissolving the ether, separates about half the gas from solution, and no effervescence was observed when the ethereal solution was thus diluted.

This excess of ratio, and the separation of oxide of zinc on the addition of water, are, after all, inconclusive grounds for assuming that some allyl-iodide of zinc is produced; and our attempts to get any indication of free zinc allyl completely failed. No fuming was ever seen, and we could separate from the ethereal solution, no organic compound, except the liquid having the properties of diallyl and the non-volatile hydrocarbon before described.

Zinc alone acts very slowly on allyl iodide in presence of ether.

Action of the Couple on Allyl Iodide and Water.

Pure granulated zinc was found to have no effect on allyl iodide in presence of water, at the ordinary temperature. Our usual zinc-foil had a little action, and the copper-zinc couple a great deal; thus in two comparative experiments, continued for 24 hours, 32 c.c. of gas were evolved by means of the former, 550 c.c. by the latter.

5 c.c. (9 grams) of the iodide were added to the ordinary quantity of the couple wet with water. There was an immediate evolution of gas, which continued for 48 hours, when 918 c.c. had been collected. The temperature was about 17°. The gas burnt with a very bright flame, dissolved readily in absolute alcohol, combined with bromine, and fuming sulphuric acid absorbed 99 per cent. of it. It needs no further proof that the hydrogenation of the C_3H_5 had not proceeded so far as to produce either dipropyl, $\left\{ \begin{smallmatrix} C_3H_7 \\ C_3H_7 \end{smallmatrix} \right.$, or propyl hydride, C_3H_8 ; but had stopped at the first stage, giving rise to the olefine, C_3H_6 , propylene.

The reaction would appear to be—

and the theoretical amount of gas producible from 9 grams would be 1200 c.c.

Action of Zinc on Allyl Iodide and Alcohol.

The couple acts so violently on iodide of allyl when mixed with alcohol, that our experiments were confined to the action of zinc alone, and even this becomes unmanageable, unless means are employed for keeping down the temperature.

5 c.c. of the iodide, with 10 c.c. of absolute alcohol, were added to 10 grams of pure granulated zinc. Evolution of gas commenced immediately. The flask was at once immersed in water at 14°, and the action ceased in six minutes, by far the greater portion of the gas having been produced in the first two minutes. The gas, collected as usual over water, measured 1035 c.c.

Alcohol of spec. grav. 0·805, was found to act more slowly, on account of the retarding influence of the water, and when it is more dilute, the water interferes with the completion of the reaction, through the formation of a crust of compact oxide on the zinc, most probably from the decomposition of the iodo-ethylate of zinc produced. (See *Journ. Chem. Soc.*, May, 1873.)

A very convenient method for preparing pure propylene is to place some granulated zinc in a flask provided with a delivery tube and thistle-funnel, cover the zinc with absolute alcohol, and add iodide of allyl, as the gas is required.* Some gas prepared in this manner was purified by passing through aqueous alcohol and water successively. It burnt with a smoky flame, combined with bromine, to form an oily body boiling pretty constantly at 143°, and dissolved rapidly and completely

* The nearest approach to this method is that of Tollens and Heiniger, only they employ hydrochloric acid in addition, which gives impure gas.

in absolute alcohol and fuming sulphuric acid. The sole reaction, therefore, with alcohol would appear to be