L.—*Researches on the Action of the Copper-zinc Couple on Organic Bodies.* Part X. *On Bromide of Benzyl.*

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.C.S., Lecturer on Metallurgy to the Medical School of the National Dental Hospital.

Our previous researches on the action of the copper-zinc couple on organic bodies of the fatty acid series enabled us to prepare several organo-zinc compounds and paraffins. We have since extended the investigation to compounds of the aromatic series, in the hope especially of preparing some organo-zinc body belonging to the phenyl group.

The existence of three isomeric bodies having the ultimate composition C_7H_7Br, namely, ortho- and para-bromotoluene and benzyl bromide, attracted our attention, especially as we thought it might be possible to throw some further light on the difference in their structure. On trying the experiment, it was found that neither ortho- nor para-bromotoluene was acted on by the copper-zinc couple either alone or in the presence of alcohol or ether. Benzyl bromide, on the contrary, was acted on by the copper-zinc couple very readily. When about 10 c.c. of the liquid were poured upon 10 grams of the couple, the bromide slowly became darker in colour, and presently fumes of hydrobromic acid were evolved. When, however, the materials were brought together in larger proportion, 100 c.c. of the bromide to 50 grams of the couple, hydrobromic acid was evolved almost immediately, the temperature rose very rapidly, and the action became explosive in character. The experiments, therefore, had to be made on comparatively small quantities. In one experiment 10 c.c. (14·3 grams) were poured upon 10 grams of the dry couple in a flask to which an inverted condenser was attached. The flask was placed in boiling water, when fumes of hydrobromic acid were copiously evolved; a violent frothing occurred in about an hour, and in two hours from the commencement of heating the action practically ceased; the dark brown mass found in the flask mixed with residual couple was treated with ether, in which it partly dissolved, the residue being soluble in benzene.

The ethereal solution contained an organic body and zinc bromide, which was separated from it by means of water, and was found to weigh 1·91 grams. The carbon compound, purified by being redissolved in ether and precipitated by water, was found to weigh

5·15 grams. It was a yellowish-red substance, resembled resin, melted at 42°, and distilled at near redness with a considerable amount of charring and decomposition. It had a faint odour suggesting that of honey. It dissolved in ether, as already stated, very sparingly in alcohol, and readily in benzene.

On combustion with copper oxide and chromate of lead, this resin-like body gave the following percentages of carbon and hydrogen:—

	I.	II.	III.	Mean.
Carbon	92·91	92·75	93·12	92·93
Hydrogen	6·87	6·96	6·88	6·90
	99·78	99·71	100·00	99·83

The body before mentioned as insoluble in ether, but soluble in benzene, was found to consist of a brownish resinoïd substance, weighing 2·46 grams; it did not dissolve either in alcohol or in ether, unless to a very small extent; it contained no zinc compound, and only a little bromine. On combustion, it gave the following percentages:—

	I.	II.	III.	Mean.
Carbon	92·14	92·19	92·01	92·10
Hydrogen	6·59	6·93	6·63	6·72
	98·73	99·12	98·64	98·82

Making allowance for the 1 or 2 per cent. of brominated compound in the second substance, these two different bodies are evidently hydrocarbons, identical, or nearly so, in composition. We are disposed to regard them both as isomerides or polymerides of the composition C_7H_6, which would require the percentages of—

Carbon	93·33
Hydrogen	6·67
	100·00

This is almost exactly the proportion of the carbon and hydrogen in the second resin, but the first contains a slight excess of hydrogen, which may possibly be due to a little dibenzyl. A substance of the composition C_nH_n would have given 7·69 per cent. of hydrogen.

A solution of the first body in benzene was examined as to its optical properties, and it was found that the specific refraction of the substance was 0·5761 for the line A, and 0·6091 for the line F. These figures are higher than those of bodies of the C_nH_n type, and support the view that the resin consists, mainly, of some body containing a larger proportion of carbon.

A very similar result was obtained when the body insoluble in ether was purified by alcohol from the brominated compound and examined optically.

That there was no complete breaking down of the aromatic compound during the violent reaction is pretty evident from the amount of the resinous bodies obtained, 5·15 + 2·46 = 7·61 grams. The theoretical amount of C_7H_6 obtainable from the original 14·3 grams of C_7H_7Br is 7·52 grams.

It appears, therefore, that by the action of the copper-zinc couple C_7H_7Br is split up into $HBr + C_7H_6$. By what intermediate steps this may take place, we have had no means of judging. The formation of zinc bromide suggests the simultaneous production of dibenzyl, $C_{14}H_{14}$. It is not difficult, however, to account for the formation of zinc bromide otherwise, seeing that we had zinc in juxtaposition with hydrobromic acid.

This C_7H_6 or $(C_7H_6)_n$ is not stilbene. Its non-crystalline character, its melting point, and its optical properties all demonstrate that. Its physical properties also distinguish it from the isomeric di-hydroanthracene and isostilbene. We propose calling it *benzylene*, a name formerly given by Wicke to his hypothetical radicle C_7H_6, and to distinguish the substance soluble in ether as α-benzylene, and that insoluble in ether as β-benzylene.

The behaviour of these two modifications with ether was closely studied under the microscope. Both of them are very brittle solids at the ordinary temperature, translucent, with a conchoidal fracture. The α-modification absorbs the vapour of ether very readily, and when treated with liquid ether the solid pieces immediately lose their form, swell, and run down into a viscid liquid, through which rise a quantity of bubbles. At the same time, some of the compound is dissolved by the ether, and separates in myriads of minute globules on spontaneous evaporation of the solvent. The specimen of the β-modification already described, showed the same properties to a smaller degree, but as it doubtless contained some of the more soluble body, a portion of it was dissolved in a little benzene and treated with a considerable quantity of ether. This produced a milky liquid from which a viscid body subsided. When dried, this became brittle, and was found no longer to absorb the vapour of ether, or to dissolve to an appreciable extent in that solvent. It dissolved very readily in benzene or chloroform. It began to soften at about 120°, becoming at a higher temperature a dark liquid which seems not to distil without decomposition. The specific refraction of this body, dissolved in benzene, was found to be 0·5664 for the line A, and 0·6016 for the line F (difference 0·0352), which confirms the composition $(C_7H_6)_n$ previously attributed to it. The force of this deduction from the optical properties lies in the fact that the specific refraction of a body of the composition C_nH_n rarely, if ever, exceeds 0·5600 for the line A, and 0·5850 for the line F, the difference being 0·0250; while all hydrocarbons in which the atoms of carbon are in excess of those of hydrogen have a higher specific refraction, and a difference between A and F of at least 0·0360.*

An experiment was made with 10 c.c. (11·03 grams) of benzyl chloride instead of bromide, poured on to 10 grams of couple. There was little or no action at the ordinary temperature for 24 hours. When heated to 70°, the action commenced with the evolution of hydrochloric acid, which for about two hours continued at a temperature of 100°. The product, dissolved in ether and treated as before, was found to consist of 1·31 grams of zinc chloride and 5·4 grams of a viscid, resin-like body. The portion insoluble in ether, when treated with benzene, gave 0·36 gram of resinous matter. The viscid body was of a reddish-brown colour, with blue fluorescence. It became liquid at 35°, at which temperature its sp. gr. was 1·106, and its spec. ref. 0·563 for A and 0·594 for F. On combustion, it gave the following results :—

	I.	II.
Carbon	91·31	90·80
Hydrogen	6·99	6·90
	98·30	97·70

It had an odour resembling that of honey; and was very readily soluble in ether. When strongly treated *per se*, it was decomposed, giving the same remarkable odour as was obtained on the distillation of the resinous bodies previously examined. It was evidently an impure specimen of benzylene. The action with the chloride was therefore analogous to that with the bromide; but there was a larger amount of bye-products.

As this benzylene is a non-saturated hydrocarbon, it was to be expected that substitution products would be easily formed from it. On treating with strong nitric acid, a nitro-compound is produced. It did not show the slightest power of crystallising. It melts easily, and at a higher temperature explodes, with the production of a great deal of carbon; it is fairly soluble in benzene or ether, and sparingly soluble in alcohol or bisulphide of carbon; it separates from all these solutions in a liquid condition at the ordinary temperature, but solidifies on standing.

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* Most of these properties of the purified β-benzylene have been added since the paper was read at the Society.

Action in Presence of Ether.

The action of the copper-zinc couple on benzyl bromide in presence of ether is very energetic, but the nature of it differs entirely from that of the couple on the compound alone. Hydrobromic acid is not evolved, nor did we find any resinous compound. Thus, when 5 c.c. (7·15 grams) of the bromide were mixed with 10 c.c. of anhydrous ether, and the mixture was added to 10 grams of the couple in a flask fitted with an inverted condenser, the temperature of the liquid quickly increased, and, though the flask was immersed in cold water, the action was over in five minutes. The solution in the flask was miscible in absolute alcohol in all proportions. When water was added either to the ethereal solution, or to the ethereal solution containing alcohol, zinc hydrate was formed, equivalent to 0·632 gram ZnO.

It is well known that water precipitates zinc hydrate from an ethereal solution of the $C_nH_{2n+1}IZn$ compounds, with the formation of the corresponding paraffin. The precipitation of zinc hydrate therefore from the ethereal solution in the above experiment naturally suggested the presence of a benzyl compound of analogous composition, that is to say, zinc bromo-benzide, C_7H_7BrZn. But if this be true, analogy requires that, simultaneously with the precipitation of the zinc hydrate, there should be formed a hydrocarbon, C_7H_8. In order to obtain conclusive evidence of the presence of this in the oily fluid referred to above, it was necessary to experiment on a larger scale. Accordingly 100 c.c. of benzyl bromide were similarly decomposed in small quantities at a time; to the joint product, water was added, and just enough hydrochloric acid to dissolve the precipitated zinc hydrate. The oily liquid which separated was washed two or three times with water, and fractionally distilled. It commenced to boil at about 40°, the thermometer rose to 280°, when a distillate was obtained which solidified in the receiver. The temperature in a little time rose beyond the limits of the thermometer, and a small quantity of a brown tarry substance distilled. By repeated fractional distillation two compounds were isolated besides this tarry body.

The first of these compounds consisted of about 20 c.c. of a very mobile liquid, which was not acted on by sodium, and had the odour of toluene. Its physical properties, as shown below, were practically identical with those of that substance, as determined from a specimen which was reputed to be chemically pure :—

Physical properties.*	Of mobile liquid.	Of pure toluene.
Boiling point	108° to 111° C.	110° to 111° C.
Specific gravity at 14°	0·8691	0·8643
Refractive index (for A) at 14°	1·4883	1·4855
Specific refraction	0·5618	0·5617
Specific dispersion	0·0464	0·0462

There seems no need of further proof that this liquid was *toluene.*

The second compound solidified, as the liquid cooled, to a mass of crystals consisting of broken prisms. It readily dissolved in hot alcohol, from which it separated on cooling, and after three or four crystallisations the crystals had the form of rhomboidal plates. On combustion with oxide of copper it gave numbers agreeing with the formula $C_{14}H_{14}$, thus:—

	Found.	Calculated.
Carbon	91·92	92·31
Hydrogen	7·85	7·69
	99·77	100·00

The specific refraction of this substance dissolved in benzene was 0·5580 for A, with a specific dispersion of 0·0440, which is in perfect accordance with the optical properties of a body of the composition C_nH_n. All these properties show that it is the known substance *dibenzyl.*

As we observed some years ago that the yield of zinc iodo-amylate depended very much on the temperature during the reaction, the experiment above described was repeated with modifications of temperature, in the hope of obtaining a larger proportion of the supposed organo-zinc body. The ratio between the bromine and the zinc in the resulting solution was determined as follows:—

Experiment.	Atomic ratio in result. Zinc : bromine.
(1.) Flask in boiling water	1 : 1·593
(2.) Flask cooled by occasional immersion in cold water	1 : 1·600
(3.) Flask in ice-cold water	1 : 1·578

The relative amount therefore was practically the same in all three cases.

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* The sp. gr. is compared with water at 4°; the specific refraction is calculated for the line A of the spectrum; the specific dispersion is the difference of the specific refractions for the lines A and H.

The results above described would appear to justify the following conclusions:—

(1.) That the action of the copper-zinc couple on an ethereal solution of benzyl bromide produces dibenzyl, zinc bromide, and zinc bromo-benzide, according to the following equations:—

$$(a.)\ 2C_7H_7Br + Zn(Cu) = C_{14}H_{14} + ZnBr_2 + (Cu).$$
$$(b.)\ C_7H_7Br + Zn(Cu) = C_7H_7BrZn + (Cu).$$

If the action were to take place exactly in the proportions of these two equations, the atomic ratio of zinc to bromine would obviously be 1 : 1·5. It appears, however, that the action takes place very nearly in the proportion of three of equation (*a*) to two of equation (*b*).

(2.) That the action of water on zinc bromo-benzide produces zinc hydrate, zinc bromide, and toluene, thus:—

$$2C_7H_7BrZn + 2H_2O = 2C_7H_8 + ZnBr_2 + Zn(HO)_2.$$

In order to satisfy ourselves that toluene was really produced by the action of the water, and in the hope of perhaps being able to effect the isolation of the zinc benzide, we acted on another 100 c.c. of benzyl bromide mixed with ether. The product was separated by filtration from the excess of couple, and distilled by heating in a bath up to 130° until the liquid ceased to come over. This portion was found to consist of ether, with a very small amount of the products of the reaction. When the distillation at this temperature had ceased, a brown viscous mass was noticed in the flask, apparently insoluble in the remaining liquid. This liquid was removed into a retort, and distilled over a lamp; an almost colourless liquid was obtained, followed by some brown tarry matters. The colourless liquid on rectification was found to consist mainly of dibenzyl dissolved in a small quantity of a liquid which boiled at a lower temperature. This liquid apparently contained traces of toluene, together with some liquid of a higher boiling point. This was found to have a sp. gr. considerably above that of water, with a comparatively low specific refraction, whilst its specific dispersion indicated that we were still dealing with bodies in which six atoms of carbon are "doubly-linked." These properties raised a suspicion that the liquid was a bromine compound. When some of it was dissolved in toluene, and heated with metallic sodium, decomposition ensued with separation of carbon, and a large amount of sodium bromide was formed. The amount of this brominated compound obtained was too small for purification, and we have not been able to satisfy ourselves whether it is the same substance which has been noticed in some of the products of this reaction, a substance having a pungent odour, and causing an unpleasant sensation in the throat, but not a flow of tears as the original bromide does. The brown viscous mass left in the flask was further distilled, but no volatile zinc compound was obtained. The ratio of zinc to bromine in it was, however, determined and found to be as 1 : 1·6, as in the previous experiments.

It would appear, therefore, that the principal organic product of this reaction is dibenzyl, formed by the direct removal of the bromine by the zinc, and partly perhaps by the destructive distillation of a bromo-zinc compound first produced.

It was found that when the products of the reaction above described were treated with two or three times their volume of anhydrous ether, a white solid substance separated. This was readily soluble in absolute alcohol; it contained both zinc and bromine. Attempts were made to analyse it, but without much success, on account of its tendency to change into another substance insoluble in alcohol; but in one case where it was washed several times with ether by decantation, the ratio of zinc to bromine was determined as 3 : 2.

Action in Presence of Alcohol.

As the zinc compound produced in the reaction in presence of ether was not decomposed by alcohol, but was broken up by water, it became necessary to see what was the action of the couple on benzyl bromide in presence of alcohol itself. The nature of the reaction was found to be very different.

In an experiment, 5 c.c. of the bromide and 10 c.c. of absolute alcohol were poured on to 10 grams of copper-zinc couple. The temperature of the liquid rose almost immediately; in three minutes it boiled, and in two more the action practically ceased. The liquid in the flask was somewhat viscous and almost colourless. The addition of water to it produced a copious separation of zinc hydrate, and on analysis it was found to contain zinc and bromine in the atomic proportions of 1 : 1·15. This near equality in the proportions of the elements shows that the action differs from what takes place in presence of ether, and suggests that it consists in the formation either of the supposed zinc bromo-benzide, or of the known zinc bromethylate, or possibly of a mixture of these bodies. The atomic proportion of zinc and bromine in either of these compounds would be 1 : 1. Supposing the action to be similar to what takes place in the fatty acid series of bodies, with the production of bromethylate of zinc, C_7H_8 would be formed thus:—$C_7H_7Br + C_2H_6O + Zn(Cu) = C_7H_8 + ZnC_2H_5OBr + (Cu)$. Supposing, on the contrary, that the bromide of benzyl simply combines with an atom of zinc, there will be no hydrocarbon separated.

In order to ascertain whether toluene was a product of this reaction, 20 c.c. of the bromide, mixed with 40 c.c. of absolute alcohol, were acted on by the couple as before. The liquid was poured off the residual couple and distilled up to a temperature of 130°. On redistillation nearly the whole of this portion passed over at the temperature at which alcohol boils (78°), but on examining it in a hollow prism, it was at once seen to be far from pure alcohol. Indeed the increased refraction and dispersion led to the belief that one-fifth of it was toluene. On the addition of water 6—8 c.c. of a clear liquid separated, which redistilled at about 111°, had a sp. gr. of 0·8610, with a specific refraction of 0·5604, and a specific dispersion of 0·0474. It was therefore pretty pure toluene. On heating the residuum in the flask at above 130°, a coloured liquid was obtained in which some dibenzyl was detected. We conclude, therefore, that the main action is that expressed by the above equation, whilst our experiments do not enable us to decide as to the presence or absence of any zinc bromo-benzide among the products.

Action in Presence of Water.

When benzyl bromide was added to a wet couple made with granulated zinc, the temperature rose slowly, and in 24 hours the action was found to be complete, with crystals of dibenzyl visible on the residual mass. The flask was then immersed in a paraffin-bath at 130°. The distillate consisted of water, a comparatively small quantity of a liquid with the specific gravity, refraction, and dispersion of toluene, and a little dibenzyl. The flask contained more dibenzyl and a small quantity of a brown resinous substance. We conclude that the action of the couple on benzyl bromide in presence of water is for the most part represented by the following equation:—

$$2C_7H_7Br + Zn(Cu) = C_{14}H_{14} + ZnBr_2 + (Cu),$$

while at the same time a portion is decomposed as follows:—

$$C_7H_7Br + H_2O + Zn(Cu) = C_7H_8 + ZnHOBr + (Cu).$$

The above research is not so complete as we could wish; but the highly painful and injurious character of the vapour of benzyl bromide, even in the smallest quantities, deterred us from continuing its examination. We believe that we have established, at any rate, some points of analogy between the action of the copper-zinc couple on members of the fatty acid and on the aromatic series, and have indicated the existence of some new compounds.