XIX.—*Note on the Action of Bromine on Benzene.*

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IN a former paper communicated to the Society (Trans., 1897, 71, 1013), one of the authors referred to a paper by Ador and Rilliet (*Ber.*, 1875, 8, 1286), where it was stated that, by the action of a small quantity of bromine on excess of benzene, bromine additive products are formed, which, on treatment with zinc ethide and subsequent oxidation yield metabromophthalic acid and metaphthalic acid. The reaction was supposed to take place according to the following equations.

(1) $C_6H_6 + Br_2 = C_6H_6Br_2$. (2) $C_6H_6Br_2 + 2ZnEt_2 = C_6H_6Et_2 + ZnBr_2$.

And on oxidation with chromic acid

$$C_6H_6Et_2 \text{ gave } C_6H_4(COOH)_2.$$

Besides the two meta-acids mentioned above, they also obtained benzoic acid, parabromobenzoic acid, and terephthalic acid, but no phthalic or orthobromobenzoic acids.

This formation of meta-compounds by direct addition of bromine to benzene is one of great interest, and the fact that no ortho-disubstitution derivatives seemed to be produced rendered it still more perplexing.

We have repeated the work of Ador and Rilliet, and find it to be substantially correct, but as we have been able to prove that ortho-di-derivatives are also produced, and that a different result is obtained when bromine and benzene are allowed to react in the dark or in sunshine, we have thought it worth while to record the facts.

The method employed by Ador and Rilliet was briefly the following. Dry benzene (200 grams) was mixed with bromine (6 grams), the mixture exposed to sunlight, the product washed with water and a little dilute soda, dried, and boiled with zinc ethide for 20 hours. The excess of benzene was then distilled off, and all that boiled above 110° was collected and oxidised with chromic acid.

Our experiments were made on a somewhat larger scale, in the hopes of obtaining perhaps enough of the ethyl compounds to separate by fractional distillation, but this was found to be impossible, as only very small quantities of the substances were produced, and the product consisted of a mixture having no definite boiling point.

Our first series of experiments consisted in allowing the dry benzene (which had been carefully prepared from pure crystalline benzene by distillation) and bromine (also purified) to remain in the dark for 24 hours. From 500 grams of benzene and 50 grams of bromine we obtained only about 7 c.c. of liquid boiling above 100°. In another experiment with the same amounts, we obtained somewhat more, but the reaction did not seem to have proceeded far, and much bromine remained unacted on. The 7 c.c. of liquid boiled between 100° and 270°, and at no point were we able to say more passed over than at any other.

The various fractions collected at 100—120°, 120—170°, 170—210°, and above 210° were separately oxidised with potassium permanganate.

The two fractions of lower boiling point gave considerable quantities of benzoic acid (m. p. 120°), but mixed with it were traces of a bromorthophthalic acid, as eosin was formed when it was heated with resorcinol and sulphuric acid. From the fraction 170—210°, we were able to isolate an acid containing bromine which melted at 248°; parabromobenzoic acid melts at 251°. A determination of bromine gave 39·0 per cent.; $C_6H_4Br\cdot COOH$ requires $Br = 39{\cdot}8$ per cent.; the amount of silver in the silver salt was also determined, Found $Ag = 37{\cdot}6$; $C_6H_4Br\cdot COOAg$ requires $Ag = 35{\cdot}6$ per cent. The amount of acid at our disposal, however, was so exceedingly small (about 0·3 gram) that we were unable to purify it properly, which fact may account for the excess of silver found in the analysis of the salt. From the fraction 210° and above, a very small amount of acid was obtained which was partly soluble in hot water; it did not give any reaction for an orthodicarboxylic acid of benzene when heated with resorcinol and sulphuric acid, it melted at 185°, and sublimed at a higher temperature. An analysis gave 39·8 per cent. of bromine, but its melting point does not agree with that of any of the bromobenzoic acids.

Our next experiments were made with the same quantities of benzene and bromine, which were carefully purified, dried, and mixed at - 10°; the mixture, after being exposed to sunlight for 6 hours, was washed with water, dried over calcium chloride, and 40 grams of zinc ethide were then distilled into the dry mixture and the whole boiled for 24 hours (3 days). The product was washed with dilute hydrochloric acid, dried, and fractionated; 34 c.c. passed over above 100°, this was separated into the following fractions, 100—120° about 5 c.c., 120—150° about 4 c.c., 150—200° about 5 c.c., above 200° about 20 c.c. These fractions were oxidised, as in the preceding case, with potassium permanganate. The first fraction gave large quantities of benzoic acid, but after evaporating the benzoic acid on the water bath, a residue was left which gave a strong fluorescein reaction with resorcinol and sulphuric acid, proving the presence of an orthophthalic acid. The second fraction gave also chiefly benzoic acid, but after this acid had been volatilised at 100°, there remained a small amount of an acid which was almost insoluble in cold water; it was soluble in ether and slightly so in hot water, and was purified by several times dissolving it in alcohol and precipitating with water. It did not contain bromine, and gave no phthalic acid reaction with resorcinol. On comparing it with isophthalic acid, it seemed identical under the microscope, both when crystallised from water and when sublimed. When the two acids were heated, they both behaved in a similar manner, melting and subliming at about 310°.

Some of the salts of this acid were compared with those of isophthalic acid; with silver nitrate it gave a white precipitate, with barium chloride a white precipitate, and with ferric chloride a reddish-brown precipitate, identical with corresponding precipitates obtained with isophthalic acid. Its silver salt gave $Ag = 57 \cdot 6$ per cent., $C_6H_4(COOAg)_2$ requiring $Ag = 56 \cdot 8$ per cent. As the only other acid that it could have been was terephthalic, pure terephthalic acid was also compared with it under the microscope, but the two appeared quite different in crystalline form. It seems certain, therefore, that Ador and Rilliet's observation was correct, and that when bromine is allowed to react with benzene in sunlight, meta-di-derivatives are formed. The only acid that could be separated from the fraction of highest boiling point was parabromobenzoic acid melting at 250°.

It appears, therefore, from these results, that when bromine is allowed to act on benzene in sunlight some dibrom-additive products are formed in very small quantities, which by the reactions employed can be converted into dicarboxylic acids of benzene; as we have obtained acids that yield fluorescein and eosin (when heated with resorcinol), parabromobenzoic acid and metaphthalic acid, it follows that bromine is capable of reacting with benzene to form ortho-, meta-, and para-compounds. The explanation of this is difficult, and seems entirely at variance with the action of bromine on bromobenzene.