LXXXVI.—*The Aluminium-Mercury Couple. Part II.*
The Action of Bromine on Organic Compounds in
presence of the Couple.

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THE action of certain substances, such as iodine, metals and their salts, as bromine carriers, is well known and fully described in the "Laboratory Methods" of Lassar-Cohn, under the heading of "Bromine Carriers" (Bromüberträger). Among the substances enumerated are aluminium chloride and bromide. Metallic aluminium has also been used in one or two isolated cases (Blümlein, *Ber.*, 1884, 17, 2486; Ris, *Ber.*, 1887, 20, 2621; Gustavson, *Beilstein's Org. Chem.*, 3rd. ed., I., 67), but as the aluminium in these cases is added to the bromine previously to introducing the organic compound, it is to be assumed that it is only a modification of the use of aluminium bromide, since aluminium and bromine would immediately react to form the bromide of the metal.

The activity of the aluminium-mercury couple in effecting combination between certain halogen compounds and the hydrocarbons suggested its application as a halogen carrier.

The following experiments show that it may be conveniently used for this purpose. The substances selected do not combine with bromine readily under ordinary conditions, but are rapidly brominated in presence of the couple. That the action is due mainly to the

couple, and not to any aluminium bromide which might be formed, is clearly indicated by the fact that the couple is scarcely attacked during the progress of the reaction.

The method is carried out as follows. A round flask to hold the hydrocarbon, or other substance, and the couple is attached to an upright condenser, the upper end of which is closed by a cork perforated with two holes. Through one of these a tap funnel for delivering the bromine is inserted, and through the other a bent tube passes, the long limb of which dips under water and absorbs the hydrobromic acid evolved. The product of the reaction is purified in the usual way.

Bromobenzene.—Fifty grams of benzene were taken, and about 0.5 gram of the couple added; sixty grams of bromine were then dropped in slowly from the tap funnel. The action proceeds vigorously, the liquid becomes warm, and volumes of hydrobromic acid are evolved. When in the course of about half an hour all the bromine has been added, the contents of the flask are shaken up with dilute caustic soda solution, the liquid dried over calcium chloride and fractionated.

Two experiments gave the following results on the first distillation:

I.	30	grams	boiling	at	140—170°	(bromobenzene)
	6	„	„		above 170°	
II.	37	„	„		at 140—170°	„
	5	„	„		above 170°	

The two higher boiling fractions were mixed and distilled, and 5 grams boiling at 150—200° were obtained. The residue did not solidify on cooling, and consequently very little dibromobenzene was present. Calculated on the bromine taken, the yield is about 60 per cent. of the theoretical amount.

Bromotoluene.—Fifty grams of toluene and 60 grams of bromine yielded, on the first distillation:

31	grams	boiling	at	180—190°	(bromotoluene)
10	„	„	„	190—200°	

The yield is about 50 per cent. of the theoretical quantity, which would no doubt be increased by further fractionation. The product is probably a mixture of the ortho- and para-compounds.

Parabromometaxylene.—Fifty grams of metaxylene and 60 grams of bromine gave, on the first distillation:

32	grams	boiling	at	185—210°	(bromoxylene)
11	„	„	„	210—230°	
5—6	„	„		above 230°	

Parabromochlorobenzene.—Chlorobenzene reacts vigorously with bromine in presence of the couple, and yields bromochlorobenzene melting at 62—63°. On recrystallising from alcohol, it melted at 65—67° (Beilstein gives 67·4°).

Bromoparachlorotoluene.—Twenty-five grams of parachlorotoluene (from paratoluidine) and 30 grams of bromine gave a bromine derivative which decomposed when distilled at atmospheric pressure. At 40 mm., it distilled as follows :

5 grams boiling at 100—120°
22 „ „ „ 120—135°

The larger fraction was redistilled, and after about 2 c.c. had passed over, it boiled steadily at 130—135°. The analysis gave the following results :

0·244 gave 0·3862 AgCl + AgBr.

$\text{CH}_3 \cdot \text{C}_6\text{H}_3\text{ClBr}$ requires AgCl + AgBr = 0·3947 gram.

Action of Bromine on Monobromobenzene.

The action of bromine on benzene previously described as yielding monobromobenzene, occurred in presence of an excess of benzene, and it was therefore interesting to find whether the action of the couple could effect further substitution.

Monobromobenzene was therefore treated with a further quantity of bromine. The action was apparently as vigorous as in the case of benzene, and the chief product was paradibromobenzene m. p. 87°. In the same way, paradibromobenzene was converted into tetrabromobenzene, m. p. 175—176° (the melting point of 1 : 2 : 4 : 5-tetrabromobenzene is given in Beilstein as 175°). With a large excess of bromine acting on the dibromobenzene, hexabromobenzene was formed. It was recrystallised from toluene, and gave the following result on analysis :

0·1520 gave 0·3060 AgBr. Br = 85·6.

C_6Br_6 requires Br = 86·9 per cent.

Action of Bromine on Bromoparachlorotoluene.

In presence of the couple, bromine acts vigorously on bromochlorotoluene, forming dibromochlorotoluene, m. p. 94°.

0·2135 gave 0·3925 AgCl + AgBr.

$\text{CH}_3 \cdot \text{C}_6\text{H}_2\text{ClBr}_2$ requires AgCl + AgBr = 0·3898 gram.

Action of Bromine on Heptane.

Seventy-five grams of impure heptane from light petroleum boiling at 95—100° and 60 grams of bromine were allowed to react in presence of the couple in the manner described; the bromine was rapidly absorbed and hydrobromic acid evolved. After distilling off the unchanged light petroleum at the ordinary pressure, the remainder was fractionated at 100 mm.

A liquid boiling at 110—120° first distilled, which is probably heptylic bromide. At this point, the distillation was stopped and the contents of the flask poured out; the liquid, on cooling, formed a mass of colourless needles having a strong camphor-like odour. The crystalline mass was separated from adhering oil by spreading on a porous plate. It consisted of two substances, which could be easily separated by means of alcohol; the compound soluble in alcohol after recrystallisation melted at 88—90°, and gave the following result on analysis:

0.1285 gave 0.2324 AgBr. Br = 76.9.

$C_7H_{12}Br_4$ requires Br = 76.9 per cent.

The substance is therefore a tetrabromoheptane.

The second product, which is only slightly soluble in alcohol, was recrystallised from glacial acetic acid. It forms colourless needles which did not melt at 250°, but on heating on platinum foil it fused and volatilised completely without decomposition, giving off a vapour having a strong odour of musk. It was analysed with the following result:

0.1327 gave 0.2379 AgBr. Br = 76.2 per cent.

It therefore contains the same amount of bromine as the previous compound, which it accompanies; from its high melting point, it may possibly be polymeric with it.

The above account is a preliminary notice, and we propose to extend the investigation, especially into the action of bromine on the paraffins, and to prepare, if possible, their higher bromine derivatives, a group of compounds which are little known.