XXII.—*Preparation and Properties of Orthochlorobromobenzene.*

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In the course of an investigation on the halogen derivatives of benzene, we have had occasion to prepare in quantity all the modifications of its di-derivatives containing chlorine and bromine.

We find that orthochlorobromobenzene has not hitherto been described, and the object of the present communication is merely to place its properties on record. The starting point of its preparation was orthonitrobromobenzene; this was made by nitrating bromobenzene in the cold in the manner described by Coste and Parry (*Ber.*, 1896, **29**, i, 788); this gave very satisfactory results, but we found it most convenient to separate the ortho- and para-compounds by grinding them up in a mortar with small quantities of cold methylated spirits and filtering, repeating the operation until the filtrate became colourless. The orthonitrobromobenzene dissolved, and after the solvent had evaporated was obtained in long needles which melted at 42° after recrystallisation.

On reducing the orthonitrobromobenzene to the corresponding bromaniline, Hübner and Alsberg (*Annalen*, 1870, **156**, 316), and later Fittig and Mager (*Ber.*, 1874, **7**, 1179), found great difficulty in obtaining the latter in the solid state; we experienced the same difficulty, which was completely overcome, however, when we added the nitrobromobenzene in alcoholic solution, instead of in the solid state, to the slightly warmed reducing mixture of stannous chloride and hydrochloric acid. On shaking vigorously, the reduction proceeded with development of heat, and after cooling, adding excess of caustic soda and distilling with steam, the oil which came over solidified in the receiver; after recrystallising, it melted at 32°.

To convert the orthobromaniline into orthobromochlorobenzene, it was diazotised in the usual manner, and the solution of the diazo-compound added to a warm solution of cuprous chloride. The oil which separated was then distilled over with steam, the distillate

extracted with ether, the extract dried over calcium chloride, and after driving off the ether the residue was fractionally distilled. The greater part came over between 200° and 202°.

The halogens were determined by Carius' method.

0·302 gave 0·5168 mixed silver haloids. $AgBr = 0·2948$; $AgCl = 0·222$.

Br = 41·52 per cent.	Found	41·77	Calculated.
Cl = 18·18 per cent.		18·53	

Orthochlorobromobenzene is a clear, straw-coloured liquid having a strong aromatic odour. It boils constantly at 204° (mercury column in vapour, pressure 765 mm.), and does not solidify at −10°. Its sp. gr. = 1·6555 at 12·5°, and μ_D = 1·583 at 15°.

For purposes of comparison, we determined the sp. gr. and refractive index of metachlorobromobenzene and found its sp. gr. = 1·6274 at 14°, and μ_D = 1·578 at 15°.

The following table gives some of the constants of the chlorine and bromine di-derivatives of benzene.

	Boiling points.			Sp. gr.		
	Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
$C_6H_4Br_2$	223·8°	219·4°	219°	1·977	1·955	—
C_6H_4ClBr	204	196	196·3	1·6555	1·6274	
$C_6H_4Cl_2$	179	172	172	1·3254	1·307	

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