LXXIX. *The Bromine Derivatives of β-Naphthol.*

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β-Monobromonaphthol is obtained in the following way. The quantities of β-naphthol and bromine calculated from the following equation are weighed out:—

$$C_{10}H_7OH + Br_2 = HBr + C_{10}H_6\left\{\begin{matrix}Br\\OH\end{matrix}\right..$$

The β-naphthol is dissolved in glacial acetic acid so as to form a tolerably concentrated solution, and the bromine is mixed with about an equal volume of glacial acetic acid. The solution of β-naphthol is first allowed to cool completely, and the flask immersed in a basin of water, while the bromine is added drop by drop from a dropping funnel, the flask containing the naphthol being shaken after each addition. The bromine is quickly absorbed, and on standing colourless needles with an adamantine lustre crystallise out. After a few crystallisations, these become quite white and pure, and are then washed from excess of acetic acid with water, and dried between filter paper. The following are the results of the analysis of this substance.

(1.) 0·2410 of the substance gave 0·0785 H_2O and 0·4740 CO_2, which corresponds with—

	Percentage found.	Calculated for $C_{10}H_6BrOH$.
Carbon	53·65	53·88
Hydrogen	3·60	3·14

(2.) 0·2100 gave 0·0585 H_2O and 0·4145 CO_2.

	Found.	Calculated.
Carbon	53·81	53·88
Hydrogen	3·09	3·14

(3.) 0·2995 gave 0·2220 AgBr, and 0·0172 Ag.

	Found.	Calculated.
Bromine............	35·79	35·78

β-Monobromonaphthol is soluble in alcohol, ether, petroleum-spirit, and benzene. It melts at 84°; if it is heated higher, at about 130° it begins to decompose, giving off fumes of hydrobromic acid, which at higher temperatures become very copious. If it is heated as long as fumes of hydrobromic acid are given off, a black resinous mass is left behind, and a very small quantity of crystalline sublimate is formed in the upper part of the tube. If it is mixed with excess of potash or soda and a small quantity of water in a flask, and heated in an oil-bath, first gradually to dryness, and then to 250°, a black mass is obtained, which dissolves when boiled with water; the solution thus formed is precipitated by hydrochloric acid. The precipitate thus obtained, when dried, gives on heating a sublimate of crystals of β-naphthol.

When it is oxidised by an alkaline solution of potassium permanganate at the heat of the water-bath, orthophthalic acid is formed. The β-monobromonaphthol is dissolved in the cold in a solution of caustic potash, a little solid potassium permanganate added, and the mixture is heated on the water-bath for about ten minutes. If the colour given to the solution by the permanganate is then quite taken away, more is added, and the heating is repeated; this is done till the colour of the permanganate remains after heating. Then ferrous sulphate is added and the mixture heated after the addition, and this is done till the colour of the permanganate is taken away. Hydrochloric acid is added till the solution is acid, and then it is extracted with ether. The ethereal solution is separated by means of a tap-funnel; and on standing, a crystalline mass is deposited from it; on heating this (after drying), colourless needles of phthalic anhydride are sublimed. The melting point is 128°.

It contains no bromine, which is shown by heating it with sodium in a tube, then dissolving the mass in water, and adding nitric acid and silver nitrate, when no precipitate is formed. It is also shown to be phthalic anhydride by heating with resorcin and then dissolving in ammonia, when the yellow solution with green fluorescence, due to fluorescine, is formed.

β-Tetrabromonaphthol, $C_{10}H_3Br_4OH$, is obtained in the following manner. β-Naphthol is dissolved in glacial acetic acid and bromine is added until it ceases to be absorbed. In order to see that enough bromine has been added, it is allowed to stand for a day, and then a small quantity of the solution is added to a solution of potassium iodide and shaken up with carbon bisulphide. If the carbon bisulphide is coloured violet with iodine, it shows that enough bromine has been added, as the unabsorbed bromine sets the iodine free. The following reaction takes place:—

$$C_{10}H_7OH + 8Br = 4HBr + C_{10}H_3Br_4OH.$$

The tetrabromonaphthol soon crystallises out, forming a mass of white needles, which is filtered off from the mother-liquor by means of the Bunsen-pump, and washed from excess of bromine with glacial acetic acid, small quantities being used at a time. Then it is recrystallised from glacial acetic acid until it is quite white, when it has a constant melting point (156°). It is then washed from acetic acid with distilled water, and dried with filtering paper.

The following are the results of the analysis of this substance:—

(1.) 0·1950 gave 0·2670 AgBr and 0·0310 Ag.

	Found.	Calculated.
Bromine	69·12	69·56

(2.) 0·2440 gave 0·0235 H_2O and 0·2385 CO_2.

	Found.	Calculated.
Hydrogen	1·06	0·87
Carbon	26·63	26·09

The tetrabromonaphthol is not so soluble in acetic acid as the monobromonaphthol. It is also soluble in carbon bisulphide, benzene, and alkalis.

I also studied the effects of the oxidation of β-tetrabromonaphthol with potassium permanganate. The process was carried on in exactly the same way as with the monobromo-compound, as described above. The ethereal extract deposited, on standing, a crystalline mass, which on heating (after drying) gave a sublimate of colourless needles. This was tested qualitatively for bromine. A small quantity of the substance was placed in a narrow tube, closed at one end, and a small piece of metallic sodium a little higher up; the tube was heated just above the sodium, which melted and ran down on to the substance, decomposing it, and forming sodium bromide. The hot part of the tube was then put into cold water, when it immediately cracked, and the water came in contact with the fused mass.

The solution gave the reaction for bromine with silver nitrate and nitric acid.

Two combustions gave the following results :—

(1.) 0·2100 gave 0·0335 H_2O and 0·3230 CO_2.

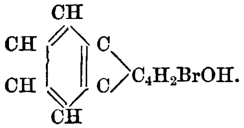
(2.) 0·2140 gave 0·0350 H_2O and 0·3280 CO_2.

	Percentage composition.		
	(1.)	(2.)	Calculated.
C	41·90	41·77	42·29
H	1·76	1·82	1·32

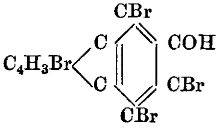
These results agree with the formula $C_8H_3BrO_3$ (the anhydride of monobromophthalic acid).

The melting point was found to be 125.°

The formation of phthalic anhydride from the monobromo-compound, and of monobromophthalic anhydride from the tetrabromo-compound, gives some insight into the constitution of these bodies. Thus it shows that in the monobromo-derivative the bromine and hydroxyl are contained in the same benzene nucleus, as shown in the following formula, as in that case only is the formation of phthalic acid possible :—



And it shows that in the tetrabromo-naphthol one benzene nucleus contains three bromine atoms and the hydroxyl, while the other contains one bromine atom, as shown in the following formula, as in that case only the formation of monobromophthalic anhydride is possible :—



β-Monobromonaphthol dissolves quietly in fuming nitric acid. On adding the solution to excess of water, a yellow resinous precipitate is formed, from which I was unable to obtain a crystallised substance. I was also unable to get a crystallised nitro-compound by adding nitric acid (both strong and dilute) drop by drop to acetic acid and alcoholic solutions of the monobromo-derivative.

This research was carried on in the University of Zürich, under the supervision of Professor Merz.