XXVII.—*A New Method of producing Carbon Tetrabromide.*

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SOME time ago, while working with a yellow naphthalene compound which I obtained from dehydracetic acid (Trans., 1893, **63**, 329), I tried the action of oxidising agents on it, in order, if possible, to convert it into a naphthaquinone. The compound being very stable and not giving any very characteristic results with the ordinary oxidising agents, I heated a small quantity of it in a test tube with sodium hypobromite solution. At once I noticed a pleasant odour, and found that a small, white, crystalline sublimate had formed near the top of the tube. On repeating the experiment with larger quantities, I obtained more of these crystals, which were easily volatile with steam.

10 grams of the naphthalene compound were, therefore, treated with a large excess of strong soda solution, and 150 grams of bromine

were carefully added through a tap funnel. The solution turned dark brown at first, and an insoluble compound was precipitated; this, however, soon dissolved, and after all the bromine had been added, the solution became light yellow; on distilling, 2—3 grams of the volatile bromine compound passed over with the steam. This was redistilled with steam, collected, and dried rapidly between filter paper. It consisted of small, white crystals with a very characteristic, sweet, and rather pleasant smell; it melted at 91—92°, and boiled without decomposing at 193—194°. It was very volatile, and if left for a short time on a watch glass, completely evaporated.

A determination of both bromine and also carbon was made.

0·400 gave 0·049 CO_2. $C = 4·5$.
0·247 „ 0·5625 AgBr. $Br = 96·9$.
CBr_4 requires $C = 4·5$; $Br = 96·4$ per cent.

As tetrabromide of carbon melts at 92·5 and boils at 193·5, there was no doubt that the volatile bromine derivative was carbon tetrabromide. On looking up the literature on the formation of tetrabromide of carbon, I could find no mention of carbon tetrabromide being formed by the direct action of hypobromite of sodium on carbon compounds, although Habermann (*Ber.*, **6**, 124) mentions that if bromoform is left in sunlight with potassium hydrate and bromine during several days, tetrabromide of carbon is formed.

After I had obtained the tetrabromide of carbon from the naphthalene derivative with such ease, I at first thought that possibly it might be the two central carbon atoms in the formula of naphthalene which, being free from hydrogen, had taken up four atoms of bromine apiece.

Other naphthalene compounds were, therefore, treated in the same way. α- and β-naphthol gave the bromide at once. And I may mention here that it is a very simple experiment and easily carried out. A small quantity of the substance to be experimented on is placed in a test tube and about 5—10 c.c. of strong solution of sodium hypobromite added. The test tube is warmed till the contents are just boiling and the thumb is placed over the mouth of the test tube whilst it is cooled under the tap. On the upper end of the tube minute crystals of the tetrabromide of carbon can be seen. In order to be sure that it was only naphthalene compounds that yielded this compound, of course I had to try others as well. Benzene and anthracene derivatives gave the bromide as well as the naphthalene compounds, and the phenols gave particularly large quantities. Next I tried derivatives of the paraffin hydrocarbons and unsaturated compounds. Whenever there was any chance of action occurring, invariably tetrabromide of carbon was produced.

To give a short list of the substances experimented on which yielded carbon tetrabromide, they are as follows:—alcohol, acetone, glycol, glycerol, mannitol, the sugars, malic acid (freely), citric acid, and apparently all unsaturated acids, oxypyridine derivatives, and all the alkaloïds that were experimented with, many benzene derivatives, especially the phenols, naphthalene and anthracene derivatives, starches, wood, cellulose, &c.

The action, therefore, seems to be a general one and of some interest.

The yield, however, is not good. In one experiment with alcohol, 2 grams of alcohol were treated with excess of sodium hypobromite, and gave on warming only 0·25 gram of the bromide. Phenols, especially carbolic acid and orcinol, give relatively large quantities, and may be used for its preparation.

The mechanism of the action is probably complex, after bromine is added oxidation takes place, and the molecule completely breaks down. Then the excess of soda probably liberates bromoform, which is further attacked by the excess of hypobromite present.

I satisfied myself that bromoform is converted into tetrabromide of carbon by sodium hypobromite by warming bromine, bromoform, and caustic soda together; the action occurs slowly owing to the insolubility of the bromoform, but after about half an hour a gram of bromoform used had been completely converted into the solid tetrabromide of carbon.

I may mention that the bromine used in these experiments was prepared from fused bromide of sodium by the action of sulphuric acid and black oxide of manganese, and further purified by distillation from strong sulphuric acid; it could not, therefore, contain bromide of carbon as an impurity.

NOTE.—Since the above was written, I have found that Wallach (*Annalen*, **275**, 147) had already noticed this method for producing carbon tetrabromide. He does not, however, seem to quite recognise that carbon tetrabromide can be prepared from such widely different substances as quinine, phenol, and cellulose.—J.N.C.