XXXVI.—*Action of Chloride of Iodine on certain Organic Substances.*

By JOHN STENHOUSE, LL.D., F.R.S., &c.

So far as I am aware, chloride of iodine was first employed to act on organic substances by Mr. J. F. Brown in 1854,* who produced, by means of this reagent, iodo-pyromeconic acid and iodomecone. The chloride of iodine which was employed in the subjoined experiments was prepared by passing chlorine into a retort containing moist iodine, care being taken to keep the iodine in excess. The product was then agitated with a considerable quantity of water, and allowed to stand some time to enable the excess of iodine to subside. The clear brownish-yellow solution of chloride of iodine thus obtained was the reagent employed.

Action of Chloride of Iodine on Orcin.

TERIODORCIN.—On adding chloride of iodine to a dilute aqueous solution of orcin, a yellowish-brown precipitate is produced, which quickly collects at the bottom of the vessel as a soft adhesive mass, which, however, on standing some time, becomes hard and brittle. Care should be taken to leave the orcin slightly in excess, by adding the chloride of iodine in quantity insufficient to precipitate the whole of it. The brownish-yellow mass thus obtained should be collected, washed with water, and dried. The dried precipitate is then dissolved in a considerable quantity of boiling bisulphide of carbon, and filtered. This separates it from a dark brown, resinous-looking substance, which remains undissolved. The greater portion of the bisulphide of carbon should then be got rid of by distillation. This is necessary, owing to the ready solubility of teriodorcin in that menstruum. The crystals obtained on the cooling of the solution are drained from the dark brown mother-liquors, and

* Phil. Mag. [4], viii, 201.

328 STENHOUSE ON THE ACTION OF CHLORIDE OF IODINE

washed with a small quantity of cold bisulphide. Having been pressed between folds of bibulous paper, they are twice recrystallised from boiling spirit of wine. The teriodorcin, as obtained by this process, crystallises in large, transparent, brittle plates, tinged with brown, somewhat resembling chloride of barium in appearance. These crystals are very soluble in bisulphide of carbon, still more so in ether, and moderately soluble in alcohol, but insoluble in water.

When heated to 100° they gradually become brown. They dissolve in caustic alkalis, decomposing, however, and yielding deep brown solutions. Strong nitric acid slowly decomposes them, even in the cold, and rapidly on heating, when nitrous fumes and the characteristic violet vapour of iodine are evolved. Sulphuric acid has no action in the cold, but on the application of heat the crystals char and give off vapour of iodine.

The crystals dried *in vacuo* over sulphuric acid were submitted to analysis, with the following results:—

- I. .365 grm. substance gave .5115 grm. AgI.
 II. .466 grm. „ „ .654 grm. „
 III. .613 grm. „ „ .370 grm. carbonic acid, and
 .065 grm. water.

			I.	II.	II.
C ₁₄	=	84	16.73	—	16.46
H ₅	=	5	1.00	—	1.17
I ₃	=	381	75.90	75.71	75.84
O ₄	=	32	6.37	—	—
		<hr/>	<hr/>		
		502	100.00		

There can be no doubt, therefore, that the substance produced by the action of chloride of iodine on orcin, is orcin $C_{14}H_5O_4$, having 3 equivalents of hydrogen replaced by iodine $= C_{14}H_5I_3O_4$, being thus perfectly analogous to the bromine-substitution-compound.

Action of Chloride of Iodine on Aniline.

When an aqueous solution of chloride of iodine containing a slight excess of iodine is added in considerable quantity to an aqueous solution of any of the salts of aniline, a copious dirty bluish-black amorphous precipitate is produced. When this precipitate is boiled with a large quantity of very dilute hydrochloric acid and filtered, the clear liquid, on being treated with an

excess of ammonia, yields a small quantity of a white crystalline precipitate. This precipitate, which is tolerably soluble in hot spirit, separates on cooling in long brilliant needles, having a slight red tinge. These crystals cannot, however, be advantageously prepared by this method, but the following process yields them readily:—Very pure nitrate of aniline is prepared by dissolving aniline boiling between 180° and 185° C. in dilute nitric acid, and subsequently crystallising several times from water and alcohol. This salt is dissolved in a large quantity of cold water, and a small quantity of a moderately strong solution of chloride of iodine is added. A bluish-green precipitate is produced, which speedily becomes almost black, closely resembling that obtained by the former process, and consisting almost entirely of amorphous substance, with a few crystals. This black precipitate is separated by filtration, and the clear pink filtrate is then again treated in a similar manner. The second precipitate is less dark-coloured than the first. After three or four partial precipitations with chloride of iodine, the product is no longer black, but of a dirty greenish tint, and distinctly crystalline. These crystals are a mixture of needles and scales. Small quantities of chloride of iodine are now successively added to the filtrate, the precipitate being collected after each addition; care must be taken, however, not to add an excess of the chloride, as this is liable to alter the nature of the product; for this reason it is advisable that the last portion which is precipitated should be rejected, or at any rate kept separate from the preceding portions. The slightly coloured and highly crystalline portions obtained after the first two or three precipitations, and previous to the last, were those which I employed in this examination. This crystalline precipitate, after being thoroughly dried at a gentle heat, is repeatedly boiled with bisulphide of carbon, which dissolves the needles, and leaves the scales, which are quite insoluble in that menstruum. The excess of the solvent is removed by distillation, and after standing for some time, the solution solidifies into a crystalline magma. This dark-coloured mass is thrown on a filter, drained from the mother-liquor, and then washed with a small quantity of cold bisulphide, by which means much of the dark-coloured substance is removed. On subsequently dissolving the partially purified crystals in boiling bisulphide of carbon, filtering from a small quantity of dark-coloured matter, which remains undissolved, and distilling off the excess of the solvent. The solution deposits crystals on cooling. These

330 STENHOUSE ON THE ACTION OF CHLORIDE OF IODINE

are freed from the impure mother-liquor by throwing them on a filter and washing them as before. A large quantity of the substance may likewise be obtained from the various mother-liquors by removing the bisulphide of carbon, and proceeding to purify the product in the manner already described. In order to render the nearly white crystals obtained by this process quite pure, they must first be boiled with a small quantity of spirit, which frees them from an adhering trace of yellowish brown substance. They are then crystallised two or three times from a large quantity of boiling spirit. As thus obtained, they consist of brilliant needles, sometimes several inches in length, and bearing a considerable resemblance to sublimed phthalic acid. The substance is insoluble in hot and cold water, slightly soluble in dilute hydrochloric acid, from which it is precipitated by ammonia; very soluble in bisulphide of carbon; sparingly soluble in ether, from which it crystallises on evaporation; but the most convenient solvent is alcohol, in which it is moderately soluble.

Strong nitric acid decomposes the crystals, even in the cold, and on heating they dissolve, and fumes of iodine are evolved. Concentrated sulphuric acid has no action on them in the cold, but on gently heating they are dissolved, and precipitated unchanged on the addition of water; if, however, the temperature be raised nearly to the boiling point of the sulphuric acid, the solution becomes purple, and violet vapours of iodine are given off. Ammonia and strong solutions of the caustic alkalis have no action on the substance, even at 100° .

The crystals, after being dried in vacuo over sulphuric acid, did not lose weight at 100° ; they were therefore submitted to analysis.

I.—·653 grm. substance gave ·798 grm. AgI.

II.—·659 " " ·805 "

III.—1·346 " " ·7765 grm. carbonic acid, and
·126 grm. water.

IV.—1·372 grm. substance gave ·7830 grm. carbonic acid, and
·136 grm. water.

V.—·849 grm. substance gave ·02827 grm. nitrogen.

VI.—1·117 grm. substance gave ·2445 grm. platinum.

	I.	II.	III.	IV.	V.	VI.
C	—	—	15·74	15·57	—	—
H	—	—	1·04	1·10	—	—
I	66·44	66·01	—	—	—	—
N	—	—	—	—	3·33	3·1

The substance employed in the above analyses was prepared at different times, and though perfectly homogeneous and in fine crystals, it was found to contain nearly half a per cent. of chlorine, which I regard as an accidental impurity. I have not been able to deduce a satisfactory formula, or to determine the atomic weight of this substance, as I have not succeeded in producing any of its combinations. It is clearly not a simple aniline substitution-compound, but probably belongs to some new class of combinations.

Oxalate of aniline when treated in a similar manner, yields the same products as the nitrate, although the latter is the best source, as the crystals obtained from it are much more easily purified. I should expect that the other soluble salts of aniline would yield the same product when treated with chloride of iodine. The compound already referred to as consisting of scales, which remains undissolved on treating the crude substance with boiling bisulphide of carbon in the preparation of the needles, occurs in comparatively small quantity, and has a purplish hue. On attempting to purify these scales by crystallising them from hot spirit, they decomposed so rapidly that, after the filtration of the boiling solution, only a small quantity crystallised out; these were now of a much paler colour, and rather grey than purple. Their most characteristic property is, that when strongly heated they fuse and then explode, giving off vapours of iodine. Owing to the very small amount of scales that can be procured by the above method, and the difficulties hitherto experienced in their purification, I have not succeeded in ascertaining their composition.

The dark-coloured amorphous substance, previously described as being obtained on the first precipitation of the salts of aniline by chloride of iodine, partly dissolves in *cold* alcohol, yielding a deep green solution, which becomes purple on the application of heat. It also dissolves in concentrated sulphuric acid with a purple colour, and is precipitated on the addition of water.

Action of the Chloride of Iodine on Salicin and Phloridzin.

If a rather strong aqueous solution of salicin be treated with chloride of iodine, and allowed to stand for some time, it solidifies to a crystalline magma of white needles. These contain iodine, but I have not yet examined them further; I could not succeed in

332 STENHOUSE ON THE ACTION OF CHLORIDE OF IODINE.

obtaining any definite crystalline compound from phloridzin by acting on it with chloride of iodine, the products being amorphous.

Action of Chloride of Iodine on Carbazotic Acid.

When carbazotic acid is dissolved in a strong solution of chloride of iodine, and digested for some hours, the solution becomes of a deep brown colour; if this be now submitted to distillation, vapour of iodine begins to arise, and a yellowish brown liquid passes over, smelling strongly of chloropicrin. After a considerable quantity of liquid has distilled, so that the solution in the retort is very concentrated, a large quantity of iodine volatilises, and is deposited in the neck. The distillation should now be stopped, the residue in the retort mixed with water, and the yellow scales which float in the liquid collected on a filter; these, after being well washed with boiling water, and recrystallised from alcohol, present all the characteristic physical properties and chemical reactions of chloranil. The absence of iodine from both compounds was ascertained. It appears, therefore, that by the action of chloride of iodine on carbazotic acid, only chlorinated products are obtained, the chief of which are chloropicrin, and chloranil, the iodine being separated in the free state.

Action of Chloride of Iodine on Benzoic Acid.

If an aqueous solution of benzoic acid be mixed with chloride of iodine solution, the former being in excess and allowed to stand for some time, the mixture gradually acquires a brown colour, and after twenty-four hours, a number of black and white crystals are deposited, the black ones being simply iodine, and the white a mixture of the chlorinated benzoic acids.

From the results of the preceeding experiments, it appears that the action of chloride of iodine on organic substances, is very variable. Sometimes the chlorine in the chloride of iodine acts merely as an introducer of the iodine into the compound; at others, the chlorine acts as when uncombined, the iodine of the chloride of iodine being separated in the free state, and remaining quite inactive.

The analyses in this paper were performed for me by my assistant, Mr. Charles Edward Groves.