

XXII.—*Researches on the Volatile Organic Bases.* By A. W. HOFMANN, Ph.D. Professor at the Royal College of Chemistry.

II.—ON THE ACTION OF IODINE ON ANILINE.

The changes which organic bodies undergo when submitted to the action of bromine and of chlorine, have of late been examined with great care by various chemists; and it must be admitted, by every body who has followed these investigations with attention, that they have thrown much light on various parts of organic chemistry.

The metamorphoses produced by these two elements, so remarkable for their powerful affinities, are generally of so strongly marked a character that, in the study of the derivatives thus obtained, the nature and constitution of a new body frequently unfold themselves in a most surprising manner. Chlorine and bromine have become in fact general agents in organic investigations. Their mode of action is known to us, based as it is, in most cases, upon their great affinity for hydrogen.

Less attention has hitherto been bestowed upon the action of iodine on organic bodies. The affinity of this element for hydrogen being much weaker, decompositions ensue with far greater difficulty.

Wöhler and Liebig, in their series of experiments on the radical of benzoic acid*—the first researches, perhaps, in which the influence of the saltformers on organic substances was investigated—found that, while part of the hydrogen in oil of bitter almonds could be eliminated with great facility by chlorine or by bromine, the corresponding iodine-compound—iodide of benzoyl—could only be obtained indirectly, viz., by the action of chloride of benzoyl on iodide of potassium, iodine being dissolved with facility in oil of bitter almonds, but no decomposition taking place. In accordance with this observation, it was established by various subsequent researches, that many organic substances by themselves may be brought into contact with iodine without undergoing the slightest change, but that decomposition can be effected with the co-operation of alkalis. In these cases, the action is a common process of oxidation, an alkaline iodide being formed, while the organic body, under the influence of the liberated oxygen, is resolved into more simple compounds. The transformations of fusel oil, by means of iodine and potash, into valerianic acid, of salicine into salicylic acid, of amygdaline into oil of bitter almonds, are well-known instances of this mode of action. To these we may add the deportment of iodine with several of

* Liebig's *Annalen*, vol. III. p. 249.

the volatile oils, such as oil of anise and fennel oil, which has only recently been investigated by Dr. Will.* Here, likewise, iodine exercises a feebly oxidising action, substances richer in oxygen but free from iodine being formed. In some cases, we also find the iodine combining with the newly-formed products; pyroxylic spirit, alcohol, citric acid, sugar, and several other substances, yield, as is well known, in this manner, iodoform with various other products.

Moreover, we have a great variety of instances in which iodine is found to combine directly with organic bodies. Whether the blue compound of iodine and starch be a chemical combination or not, the entrance of iodine in this case is certainly not accompanied by an elimination of hydrogen; and we can scarcely adopt any other view respecting iodide of elayle, if we take into consideration the mode of formation of this body, and the facility with which it is again resolved into iodine and olefiant gas.

Analogous facts have been elicited with reference to the deportment of iodine with organic bases, which has been the subject of several investigations. Pelletier,† who first directed his attention to this question, arrived, by a series of experiments on strychnine, brucine, quinine, and cinchonine, at the conclusion that these bases were capable of combining directly in various proportions with iodine, an opinion which appeared to be confirmed by some subsequent experiments of Regnault.‡ The products thus obtained would correspond to the combinations of iodine with ammonia, described by Gay-Lussac, Bineau, and Millon. The analytical numbers given in Pelletier's investigation are, however, very unsatisfactory, and Regnault has paid but little attention to the subject.

The same question was again taken up by Bouchardat.§ According to whose experiments, the details of which, however, do not appear ever to have been published, these products should be considered as combinations of the hydriodates with iodine, whose representative in the ammonium series we find to be iodinated iodide of ammonium. It is possible that *both* classes of compounds exist: the subject requires further investigation.

If all the researches on the action of iodine on organic substances be glanced over, it will be found that there is scarcely a single instance known, in which iodine does, like chlorine and bromine, eliminate and replace hydrogen, the fundamental properties of the compound

* Liebig's Annalen, vol. LXV. p. 230.

† Annales de Chimie et de Physique, 2ème sér. LXIII. p. 164. Liebig, Annalen, vol. XXII. p. 113.

‡ Ann. der Chemie Pharm. vol. XXIX. p. 58.

§ Comptes Rendus, t. IX. p. 475.

remaining unaltered. These considerations gave rise to some experiments on the behaviour of iodine with aniline, which I wish to communicate to the Society in the following pages.

The action of chlorine and bromine on aniline, as is well known, is very powerful. By their agency, it appears, that those products of substitution only can be obtained in which the whole of the replaceable hydrogen in the original aniline has been eliminated, and which have lost their basic properties. The anilines in which a smaller quantity of hydrogen is substituted, have, however, likewise been obtained by other processes, viz., by the action of alkalies on chlorinated and brominated isatine.*

The adoption of a similar method seemed to promise the preparation of iodinated aniline. Iodisatine, however, being as yet unknown, and considering the far less powerful affinity of iodine for hydrogen, I resolved to ascertain whether the desired object might not be accomplished by the direct treatment of aniline with iodine.

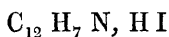
Action of iodine on aniline.—Iodine dissolves in anhydrous aniline, forming a dark brown liquid, and a rapid evolution of heat indicates at once a lively chemical reaction. If an excess of iodine has been avoided, long needles soon appear, surrounded by a brown mother-liquor. These crystals are exceedingly soluble in water and in alcohol, but less so in ether, by which liquid they may be separated from a great portion of the mother-liquor. Solution in water and ebullition with animal charcoal, and subsequent recrystallization, render them perfectly pure. The quantitative analysis proves them to be pure hydriodate of aniline.

This salt not having been previously analyzed, an iodine determination was made,

0·2856 grm. of hydriodate of aniline gave

0·3025 grm. of iodide of silver.

The formula



requires

	Theory.		Experiment.
1 equiv. of aniline	93·00	42·21	—
1 equiv. of hydriodic acid . .	127·36	57·79	57·53
1 equiv. of hydriodate of aniline	220·36	100·00	

The dark brown mother-liquor of this salt is a mixture of various substances: it contains, besides, some hydriodate of aniline, a certain

* Memoirs of the Chemical Society, vol. II. p. 266.

quantity of free iodine, which can be removed by alkalies, a brown product of decomposition, insoluble in acids and in alkalies, containing both aniline and iodine, and, lastly, the hydriodate of an iodinated base, to which, from its composition, the name of *iodaniline* belongs. The separation of the latter is easily effected by means of hydrochloric acid.

Preparation of iodaniline.—Anhydrous aniline is intimately mixed with one and a half times its weight of iodine. The brown liquid thus obtained solidifies after a very short time into a crystalline mass containing the above-mentioned substances, among which, however, iodaniline greatly preponderates. On the addition of common hydrochloric acid (sp. gr. 1.11) to this mass, the hydriodates are decomposed, difficulty soluble hydrochlorate of iodaniline remaining in the residue, while hydrochlorate of aniline enters into solution. Hydrochloric acid of greater strength should be avoided, as it would precipitate likewise some hydrochlorate of aniline. The salt, which is still much coloured, having been washed with hydrochloric acid for a short time, is now dissolved in boiling water: this solution deposits, on cooling, beautiful ruby-red very distinct crystals of hydrochlorate of iodaniline, containing still a certain amount of free iodine. By repeated crystallizations from boiling water, these crystals become constantly paler, part of the free iodine remaining each time in solution. It is scarcely probable that these coloured crystals are combinations of hydrochlorate of iodaniline and iodine in chemical proportions. I have not, however, any experimental evidence to the contrary. Possibly some of Pelletier and Bouchardat's compounds may be of a similar kind. It is scarcely possible to remove entirely the free iodine, which adheres to them with great pertinacity by mere crystallization; it may be separated, however, with facility by treatment with animal charcoal. By this process, not only the iodine, but also the brown product of decomposition is nearly altogether removed. A colourless solution is obtained, which, filtered while hot, deposits, on cooling, a large quantity of iridescent plates of a hydrochlorate, very similar in appearance to benzoic acid.

On the addition of caustic ammonia to a solution of this salt, a beautifully white precipitate of iodaniline is obtained, which is, however, not yet absolutely pure; it is still contaminated with small quantities of a yellowish substance, containing iodine, (frequently also with traces of phosphate of lime from the charcoal), from which it may, however, easily be separated by solution in alcohol, in which this yellow substance is quite insoluble. On mixing the alcoholic solution with water, a white crystalline mass of perfectly pure

iodaniline is instantly thrown down ; by evaporation on a water-bath, the base is separated in the form of yellow oily drops, which soon solidify to a crystalline mass.

The brown mother-liquor, filtered from the crude hydrochlorate of iodaniline, deposits, after a time, large crystalline plates, of an emerald-green colour, which possess the peculiar metallic lustre of the wing-covers of certain beetles. These crystals remain perfectly unaltered while in contact with the acid mother-liquor, but cannot be dried without undergoing change. The hydrochloric liquid being drained from them, they instantly become brown on exposure to the air. On the addition of water, the greater portion is rapidly dissolved, forming a light brown solution, on which a few oily drops still float. If this solution be boiled with animal charcoal, it becomes colourless, and deposits, on cooling, crystals of pure hydrochlorate of aniline, mixed perhaps with a small quantity of hydrochlorate of iodaniline.

I could not find a method of procuring the green crystals in a state fit for accurate analysis. In order to obtain an idea of their nature, some of the crystals were rapidly collected, purified and dried, as far as was practicable, by pressure between folds of bibulous paper, and kept in vacuo for a few days, when a small quantity of iodine was evolved. The solution of the substance thus prepared, was treated with hydrosulphuric acid, to convert the last trace of iodine into hydriodic acid, it was then boiled and thrown down with nitrate of silver. The precipitate was chloride of silver, mixed with traces only of iodide.

0.3200 grm. of the emerald crystals gave

0.3323 grm. of silver-salt.

If the silver-salt had been pure chloride of silver, the crystals would contain 25.68 per cent of chlorine, the amount in hydrochlorate of aniline being 27.41 per cent.

From this approximative analysis, as well as from the general behaviour of the crystals, it is evident that they are in fact nothing but hydrochlorate of aniline, which have carried down a small quantity of iodine,* by which their beautiful appearance is produced.

Among the products of the action of iodine on aniline, I have mentioned several times a brown compound containing aniline

* In an analysis of this kind, the determination by means of nitrate of silver should have yielded rather an excess of chlorine, the small quantity of iodine having been calculated as chlorine. The presence, however, of a small amount of hydrochlorate of iodaniline (containing only 13.93 per cent of chlorine,) and the incompleteness of the method of desiccation, are sufficient to explain the small loss in the analysis.

and iodine, which is insoluble in acids and in alkalies. This substance is likewise insoluble in water. Alcohol and ether dissolve it; but it does not crystallize from any of these solutions; it is not volatile without decomposition. As nothing evinced the individuality of the substance, I did not investigate it any further.

Composition of iodaniline.—The analysis of iodaniline did not present any difficulties. Two determinations of the carbon and hydrogen, with one estimation of the iodine, were sufficient to establish the composition of the new body.

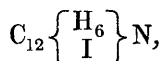
By burning the substance with oxide of copper, the following results were obtained :

- I. 0·4144 grm. of iodaniline gave
 0·5000 „ „ carbonic acid and
 0·1055 „ „ water.
 II. 0·2149 „ „ iodaniline gave
 0·2621 „ „ carbonic acid and
 0·0553 „ „ water.
 III. 0·4970 „ „ iodaniline converted into iodide of calcium by
 combustion with lime and precipitated by nitrate of silver,
 gave :
 0·5335 grm. of iodide of silver.

Per centage composition :

	I.	II.	III.
Carbon . .	32·90	33·26	—
Hydrogen . .	2·82	2·85	—
Iodine . . .	—	—	57·87

These numbers exactly represent the composition of moniodaniline



as the following comparison with the theoretical numbers will show :

	Theory.		Experiment.
12 eq. of carbon . . .	72·00	32·97	33·08
6 „ of hydrogen . . .	6·00	2·74	2·83
1 „ of iodine . . .	126·36	57·86	57·87
1 „ of nitrogen . . .	14·00	6·43	—
1 „ of iodaniline . .	218·36	100·00	

The correctness of this formula was satisfactorily controlled by

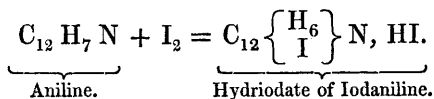
several determinations of the equivalent of the base as resulting from the analysis of its various salts.

Two determinations of platinum in the platinum-salt, which I shall mention hereafter, gave a mean per centage of 23.14 of platinum.

Equivalent by experiment 220.26

Equivalent by theory 218.36

The formation of iodaniline is effected by a simple process of substitution :



Properties of iodaniline.—Iodaniline resembles aniline in most respects, and is even more similar to chloraniline and bromaniline. It is characterized by the same pleasant, somewhat vinous odour, the same aromatic and burning taste, the same solubility in alcohol, ether, pyroxylic spirit, acetone, bisulphide of carbon, and fatty and ethereal oils. In water it dissolves but very little. These solutions have not the slightest action on vegetable colours. Iodaniline is heavier than water.

When I first obtained this compound, I expected to see it crystallize in octohedrons, an anticipation which appeared to be supported by the crystalline form of chloraniline and bromaniline, and the generally assumed isomorphism of chlorine, bromine and iodine. But I have vainly searched the different crystallizations of iodaniline for octohedrons; from all the solutions which I tried, iodaniline was invariably deposited in prismatic crystals; from a boiling aqueous solution, it separates after some time in long hair-like needles. The crystalline mass obtained by the solidification of the fused base likewise exhibited no cleavage of an octohedron.

The crystals of iodaniline fuse far below the boiling-point of water into a yellow oil. A small quantity of this substance, heated in a water-bath, was completely fused at 60° C. (140° F.); at the moment of solidification the thermometer indicated 51° C. (124° F.). Sometimes the base remains liquid for a long period, even at common temperatures; it is then usually solidified at once by agitation. At higher temperatures iodaniline may be volatilized without much decomposition. With the assistance of aqueous vapour, it distils with the greatest facility. The vapour of the base burns with a brilliant smoky flame.

Like aniline and its chlorinated and brominated relatives, iodani-

line imparts an intense yellow colour to fir-wood and the pith of the elder-tree ; but it does not communicate the characteristic violet colour to hypochlorite of lime ; a solution of this reagent on being mixed with iodaniline assuming only a slight red tint ; nor is the aqueous solution altered by chromic acid. The dry and fused substance, however, when in contact with solid chromic acid, is destroyed with violence, but not inflamed like aniline and brom-aniline.

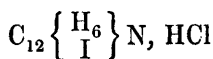
Compounds of iod'aniline.—The salts of iodaniline crystallize with the same facility as those of aniline. They are generally less soluble than the latter. By the entrance of iodine, the basic properties of aniline have been considerably weakened. A solution of aniline in water decomposes the salts of iodaniline with facility, and whilst aniline precipitates several metallic oxides, iodaniline is only capable of displacing alumina from its salts. The salts of oxide of zinc and sesquioxide of iron are not decomposed by iodaniline. With sulphate of copper a yellowish precipitate is produced, which is evidently a double salt.

Hydrochlorate of iodaniline.—This salt is but slightly soluble in cold water. The aqueous solution is precipitated nearly entirely by concentrated hydrochloric acid. From boiling water the salt crystallizes in plates or thin broad needles, which dissolve in alcohol, but are insoluble in ether.

Analysis gave the following results :

0·4531 grm. of hydrochlorate of iodaniline.
0·2573 „ of chloride of silver.

The formula :



requires the following numbers :

	Theory.		Experiment.
1 equiv. of iodaniline	218·36	85·69	—
1 „ „ hydrochlorate acid . . .	36·50	14·31	14·44
1 „ „ hydrochlorate of iodaniline	254·86	100·00	

Hydrobromate of iodaniline.—This salt resembles the preceding in every respect.

Hydriodate of iodaniline forms a radiated crystalline mass, far more soluble than the preceding salts. It is very rapidly, decomposed.

Sulphate of iodaniline.—This salt crystallizes in white brilliant scales. With respect to its solubility, it resembles the hydrochlorate precisely. The solution of this salt appears to be decomposed by ebullition; there remains, at least, a small quantity of a substance, which is completely insoluble in water.

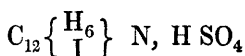
Three determinations of the sulphuric acid, in specimens of different preparations, gave a slight excess above the theoretical quantity.

I.	0.5249	gram.	of	sulphate	of	iodaniline	gave :
	0.2367	"	"	"	"	barytes	
II.	0.3440	"	"	"	"	iodaniline	gave:
	0.2037	"	"	"	"	barytes	
III.	0.3440	"	"	"	"	iodaniline	gave :
	0.1577	"	"	"	"	barytes	

which quantities afford the following per centage :

	I.	II.	III.
Hydrate of sulphuric acid	18.94	19.56	19.24

The formula :



requires

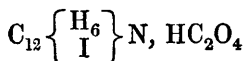
	Theory.		Mean of experiments.
1 equiv. of iodaniline	218.36	81.68	—
1 " " hydrate of sulphuric acid	49.00	18.32	19.24
1 " " sulphate of iodaniline .	267.36		

Oxalate of iodaniline.—This salt forms splendid long, flattish needles, which, like the hydrochlorate, are difficultly soluble in water and in alcohol, and insoluble in ether.

The analysis of this salt gave the following results :

0.5020	gram.	of	oxalate	of	iodaniline	gave
0.0969	"	"	carbonate	of	lime.	

The formula :



requires the following numbers :

	Theory		Experiment.
1 equiv. of iodaniline	218.36	82.92	—
1 " " hydrate of oxalic acid. .	45.00	17.08	17.37
1 " " oxalate of iodaniline .	263.36	100.00	

Nitrate of iodaniline.—This salt crystallizes from water in beautiful hair-like needles, often some inches in length. It is more soluble in water, especially when boiling, than any other salt I have examined. It is likewise easily soluble in alcohol and in ether. Its solution is not precipitated by nitrate of silver.

Bichloride of platinum and iodaniline.—The hydrochlorate of the base yields a beautiful orange-yellow crystalline precipitate with bichloride of platinum, which may be easily purified by washing with ether.

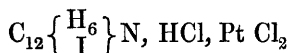
The following are the experimental numbers obtained by analysis :

I.	0.2675	gram. of platinum-salt gave :
	0.1650	„ „ carbonic acid, and
	0.0451	„ „ water.
II.	0.2771	„ „ platinum-salt gave :
	0.0643	„ „ platinum.
III.	0.1218	„ „ platinum-salt gave :
	0.0281	„ „ platinum,

per centage, composition :

	I.	II.	III.
Carbon	16.82	—	—
Hydrogen	1.87	—	—
Platinum	—	23.20	23.07

corresponding exactly with the formula :



as may be seen from the following table :

	Theory.		Experiments.
12 equiv. of carbon . . .	72.00	16.95	16.82
7 „ „ hydrogen . . .	7.00	1.64	1.87
1 „ „ nitrogen . . .	14.00	3.29	—
1 „ „ iodine . . .	126.36	29.79	—
3 „ „ chlorine . . .	106.50	25.09	—
1 „ „ platinum . . .	98.68	23.24	23.14
„ „ platinum-salt . .	424.54	100.00	

A solution of hydrochlorate of iodaniline yields a scarlet precipitate with bichloride of gold, which is, however, rapidly decomposed.

The following table embraces the iodaniline compounds which have been analysed :

Iodaniline	$C_{12} \left\{ \begin{smallmatrix} H_6 \\ I \end{smallmatrix} \right\} N$
Hydrochlorate of iodaniline . .	$C_{12} \left\{ \begin{smallmatrix} H_6 \\ I \end{smallmatrix} \right\} N, H Cl$
Sulphate of iodaniline . . .	$C_{12} \left\{ \begin{smallmatrix} H_6 \\ I \end{smallmatrix} \right\} N, H SO_4$
Oxalate of iodaniline . . .	$C_{12} \left\{ \begin{smallmatrix} H_6 \\ I \end{smallmatrix} \right\} N, H C_2 O_4$
Platinum salt	$C_{12} \left\{ \begin{smallmatrix} H_6 \\ I \end{smallmatrix} \right\} N, HCl, Pt Cl_2$

Products of decomposition of iodaniline.—The metamorphoses which the iodinated base undergoes, when treated with various chemical agents, are very analogous to those of aniline ; I have consequently studied them but cursorily.

Iodaniline, when gently heated with *potassium*, is decomposed with violence ; iodide and cyanide of potassium being produced.

A concentrated aqueous, or alcoholic solution of *potash* has no effect on iodaniline, not even at the boiling temperature.

Chlorine gives the same products with iodaniline, as with aniline itself ; viz., trichloraniline and chlorophenisic acid. The iodine, in this case, is evolved in the form of chloride.

Bromine acts in a similar manner. On adding a few drops of bromine to an alcoholic solution of iodaniline, a crystalline mass is produced, which is pure tribromaniline, the whole of the iodine being evolved in the form of bromide.

In order to establish this fact, a bromine determination of the tribromaniline thus formed was made.

0·1200 grm. of substance, heated with lime, &c., gave :

0·2076 ,, ,, bromide of silver.

	Theory.	Experiment.
Per centage of bromine in tribromaniline . .	72·28	72·68

This result was to be expected. In inorganic chemistry, we always find iodine expelled by chlorine and bromine. And among organic substances, similar cases have also been observed. According to Bouchardat's experiments, iodoform is easily converted into chloroform or into bromoform, when acted on by chlorine or by bromine.

A mixture of *chlorate of potash* and *hydrochloric acid* convert iodaniline into chlorokinone (chloranil) and chlorophenisic acid.

Iodaniline is rapidly destroyed by boiling *nitric acid*. In this pro-

cess the iodine is set free, and from the solution, scaly crystals of nitrophenisic acid are deposited on evaporation.

One peculiar decomposition I have still to mention.

Chemists are acquainted with the ingenious process which was devised by M. Melsens for substituting hydrogen in the place of chlorine in chloracetic acid. This acid, dissolved in water, is treated with a weak amalgam of potassium, and whilst the chlorine atoms are seized, as it were, by a portion of the potassium, the empty spaces become occupied by a corresponding number of atoms of hydrogen, liberated by the action of the same metal on the water. This process promises to become particularly important when employed in cases where the hydrogen term is still wanting. When Dr. Kolbe was in London, we made a few experiments of this kind together. Amongst other substances, we acted with amalgam of potassium on chloraniline and bromaniline, which, as was to be expected, are re-converted into aniline with the greatest facility. M. Melsens told me, that in performing the same experiments, he arrived at the same results.

Iodaniline I find likewise undergoes a similar change. The nitrate of this base, when brought into contact with amalgam of potassium, is at once decomposed, and the solution yields immediately a yellow precipitate with nitrate of silver. Only a small quantity, however, of aniline is reproduced in this process: the larger portion undergoes a further change, being converted into a yellow crystalline compound, of aromatic odour, the composition of which I have not yet ascertained.

The reproduction of aniline from iodaniline succeeds also with nascent hydrogen only. For effecting this, it is sufficient to heat an acid solution of sulphate of iodaniline, with some scraps of zinc, for a few minutes; starch paste indicates at once the liberation of iodine in the solution, while the addition of potash, and agitation with ether, separates the aniline, which may now be detected by a solution of hypochlorite of lime.

The action of *chlorine*, *bromine*, *iodine* and *cyanogen* on aniline, affords an interesting illustration of the decreasing affinities which these radicals manifest for hydrogen.

By treating aniline with *chlorine*, the molecular arrangement of this body is nearly entirely destroyed; almost the whole is converted into chlorophenisic acid, a body only loosely connected with the original atom, while very small quantities of neutral trichloraniline are formed.

Bromine likewise acts very powerfully on aniline ; yet its action is limited to a process of substitution, not less than three equivalents of hydrogen being replaced by bromine, in the formation of neutral tribromaniline.

With *iodine*, as we have seen, we may obtain a compound in which only one equivalent of hydrogen is replaced by iodine, the product retaining the basic properties of the original atom.

Cyanogen, finally, is no longer capable of eliminating hydrogen. It directly combines with aniline, producing a compound in which the original character of aniline has not been altered.

June 19, 1848.

John Thomas Cooper, Esq., Vice President, in the chair.

Mr. Thomas Taylor exhibited and described a small hot-air chamber, which he had devised for the purpose of drying precipitates, &c., in the laboratory.

The following papers were read :