February 3, 1845.—Robert Porrett, Esq., Treasurer, in the Chair.

Dr. Draper of New York, presented his work on the Chemistry of Plants to the Society's Library.

Messrs. Johnson and Cock exhibited Specimens of pure Palladium in its forged, rolled and finely laminated state, the former a mass weighing 100 ounces.

W. A. Gibbs, Esq., W. T. Rickard, Esq., and Robert Smith, Ph.D. were elected Members; and Mr. Joseph Cooper an Associate of the Society.

The following communication was then read:—

CXXIX. *On the Metamorphoses of Indigo.*

Production of Organic Bases which contain Chlorine and Bromine. By Dr. AUGUST WILHELM HOFMANN, Assistant in the Giessen Laboratory.*

THE changes which result from the action of various bodies upon indigo have for a series of years engaged the attention of chemists. It may be even said that this subject has been selected with preference for investigation; and when we consider the rich harvests already obtained by a great number of celebrated chemists, there would appear, at the first glance, scarcely anything to be gleaned. It is however the character of every rapidly-advancing science, that each discovery becomes the source of numerous others, and that the solution of every question gives rise to others which must in their turn be answered. It was thus that the further investigation of the products from the decomposition of indigo, which had been already so thoroughly studied in many points by Laurent and Erdmann, led to results which appeared to me worthy of publication.

Before proceeding, however, to the description of these results, it may be advantageous to make a few preliminary observations for the purpose of showing the reasons for which these investigations have been undertaken.

Among the various theories which have of late years claimed the attention of chemists, that of substitution occupies a very prominent place. It is not my intention to examine the numerous phases of this discussion, for the most part carried on in France, nor to consider minutely the various consequences which had their rise in this originally extremely simple question. The problem which forms the basis of the present investigation is a more general experimental establishment of a single substitution theorem.

If we examine carefully the origin of the theory of substitutions, we shall be able to trace it to the endeavour to predetermine, by means of certain laws experimentally established, the changes to be produced upon a body through the action of chlorine, bromine, oxygen, &c. In the course of such investigations it was however perceived, that in order to foretel these changes a complete knowledge of the constitution

* I have had the pleasure of witnessing the care and accuracy with which the author of this paper has proceeded in making his observations and establishing his facts.

It appears to me that he has produced a definite and irrefragable proof that the chemical character of a compound does not depend, as the electro-chemical theory supposes, upon the *nature* of the elements it contains, but solely on the manner of their grouping.—JUSTUS LIEBIG.

of the original body was necessary, and that this must be included in the argument. This discussion is not yet terminated, nor are we at present in a position to give an opinion as to its final result; this however is certain, that it has been the means of originating many excellent investigations, from which science has derived the greatest advantage.

It is now eight years since Laurent was led by a series of experiments to a peculiar mode of representing the action of chlorine on organic bodies, and among other views, of which we do not require here to speak, he laid down the following law :—

“ In many organic compounds, by the action of chlorine, a certain number of equivalents of hydrogen are eliminated in the form of hydrochloric acid ; the eliminated hydrogen being replaced by a like number of equivalents of chlorine, in such a manner, that the chemical character and the fundamental properties of the original compound are not sensibly altered. The chlorine molecules therefore must take the place of the hydrogen molecules, and play in the new compound the same part which was performed by the hydrogen molecules in the original.”

The ideas of Laurent, which were opposed to the electrochemical theory, and to the views generally received at that time, found, as might be expected, but an indifferent reception from chemists at the period of their publication. His views were reproached with being supported by too small a number of facts ; even his facts were assailed, and the author required all his dexterity and steady perseverance to defend himself against his powerful opponents. He repeated many of his former experiments, and added by further investigations new proofs to those already given. Since that time a mass of facts has been observed which unequivocally support the ideas of Laurent. The discovery of chloracetic acid by Dumas, the investigations of Regnault on the action of chlorine on the *Liqueur des Hollandais*, of Malaguti on the action of the same body on the compound æthers, the extended works of Laurent on the naphthaline and phenylé series, the researches of the same chemist and of Erdmann on indigo, have given so many instances in which any other view is inadmissible, that it would appear scarcely necessary to undertake still further investigations in its support.

On examining however more closely the bodies in which hydrogen has hitherto been replaced by chlorine in the way mentioned, it is found that they consist of indifferent bodies, or acids, or their compounds with æther. Up to the present time the theory of substitution remains unrepresented by a

large and important class of bodies. *No organic base* is known in which the hydrogen has been replaced by chlorine in the above-mentioned manner.* And yet it would be an argument of the greatest weight, were chlorine, an electro-negative element, to be introduced into a compound possessing electro-positive properties, without however changing its chemical character.

The above considerations induced me to undertake the following research.

The action of chemical agents in general upon the organic bases has been as yet but little studied. For the first accurate account of the special action of chlorine and bromine on these bodies, we are indebted to Pelletier †, who investigated the behaviour of strychnine toward chlorine, and at the same time communicated some details on the influence exercised by this body on quinine, cinchonine, brucine, morphine and narcotine. From his experiments he ascertained that chlorine withdrew from these bases hydrogen in the form of hydrochloric acid, and gave rise to neutral compounds difficult of solution in water, but soluble in alcohol. On submitting the crystalline product obtained from strychnine to analysis, the presence of chlorine in its composition was ascertained. Of the other bases, only quinine and cinchonine offered products of a somewhat crystalline structure. The physical properties of these substances however rendered their analysis so difficult, that we are still in the dark as to the relation which exists between them and the original compounds.

Lately Brande and Leben ‡ made some experiments on the action of chlorine on quinine, and described the various products—dalleiochine, rusiochine and melanochine, which all contain nitrogen but no chlorine. The properties of these bodies are not however well-defined, nor do their analyses bear the stamp of exactness, so that science has gained but little by their investigation. The same may be said of the researches of M. André § on the same subject.

All these details relate to solid crystalline bodies. As to

* By organic base, in the strict sense of the word, I understand here, with Liebig, that class of compound, azotized bodies, which possess all the properties of basic metallic oxides. The oxides of ethyle, methyle, &c., are not included, as the most common character of salts is wanting in their compounds, viz. the replacement of their acids by other acids, and their bases by other bases.

† *Journal de Pharmacie*, Avr. 1838, and Liebig's *Ann.*, Bd. xxix. S. 48.

‡ *Archiv der Pharmacie*, Bd. xvi. S. 257, and Liebig's *Ann.*, Bd. xxxii. S. 270.

§ *Ann. de Chem. et de Phys.*, t. lxxi. p. 195, and Liebig's *Ann.*, Bd. xxxii. S. 273.

volatile bases, all that we know is, that nicotine and coneine are decomposed by the action of chlorine, but no investigation has as yet been made of these products of decomposition.

On the other hand, there exist some accounts of the products obtained by chlorine and bromine from aniline, that artificial base which has of late been met with under so many different circumstances. These bodies crystallize, but they no longer possess the character of basic compounds.

I have myself communicated some observations on the action of chlorine on aniline, made during an investigation of the organic bases of coal-gas naphtha*. I could not at that time obtain a chlorinated basic product of decomposition from aniline. Besides a neutral compound, which was not produced in sufficient quantity for analysis, there was always formed as the chief product chlorindoptinic acid (chlorophenissic acid of Laurent), whose relation to aniline is shown by the following formula :

The action of bromine on aniline, investigated by Fritzsche†, is much less energetic. A simple substitution of bromine for hydrogen takes place, giving rise to the compound named by him bromaniloid,

But this compound too is no longer basic, but neutral, the positive properties of aniline being removed by the entrance of the electro-negative element into its composition. In these cases the action of chlorine and bromine has evidently gone too far for the aniline still to preserve its original character, and it remained therefore to try in some way to regulate the action of the above-named agents, so as to produce compounds in which only one equivalent of hydrogen was replaced, and which, like aniline, might possibly possess basic properties.

The remarkable facility with which the derived members of the phenyl family, viz. the chlorinated phenylic acid, as well as bromaniloid, crystallize, made it probable that the

* Liebig's *Annalen*, Bd. xlvii. S. 68, and Phil. Mag. vol. xxiv. p. 115.

† *Bullet. Scient. de St. Pétersb.*, 1843, t. i. p. 30, and Liebig's *Ann.*, Bd. xlv. S. 291.

270 Dr. Hofmann on the *Metamorphoses of Indigo*.

desired compound would likewise be crystalline, by which the investigation would be rendered essentially easier. I resolved therefore to make my experiments in this direction.

ACTION OF CHLORINE ON ANILINE.

I began by carefully repeating my earlier experiments, but obtained exactly the same results.

As the action of chlorine on aniline immediately forms hydrochloric acid, I chose a solution of the base in this acid, and passed through it slowly a stream of the chlorine. After a few moments the fluid became violet, thickened and deposited a brown resinous matter, which fell to the bottom of the vessel. On submitting the whole fluid to distillation, a crystalline substance was deposited in the neck of the retort in the form of white needles, consisting of a mixture of two different bodies, which are easily separated by a second distillation with potash; an indifferent crystalline substance passes over, of which I shall immediately speak, and chlorophenissate of potash remains in the retort. The resinous matter submitted alone to distillation gave likewise a large quantity of chlorophenissic acid.

In no case could I obtain any other results than the above, however much I modified my experiments by employing a more or less diluted solution, and substituting a watery solution of chlorine instead of the gas. I soon found that the desired end could not be attained in this direct way, and had consequently to have recourse to an indirect method.

Aniline, originally discovered by Unverdorben* among the products of distillation of indigo, was afterwards produced by Fritzsche† on submitting anthranilic acid to the same process, and by Zinin‡ through the action of sulphuretted hydrogen on nitrobenzid. The idea occurred to me to try the action of chlorine on anthranilic acid, and should it so happen that in this way out of the anthranilic acid $C_{14}H_7NO_4$ by the substitution of chlorine, a compound, $C_{14}\left\{\begin{smallmatrix} H_{7-n} \\ Cl_n \end{smallmatrix}\right\}NO_4$ §, could be obtained possessing the properties of anthranilic acid, it was highly probable that by its distillation the desired base would be obtained. It was also probable that by the action of chlorine on nitrobenzide, $C_{12}H_5NO_4$, it would like-

* Poggend. *Ann.*, Bd. viii. S. 397.

† *Bul. Scient. de St. Pétersb.*, t. vii. No. 12, and t. viii., and Liebig's *Ann.*, Bd. xxxvi. p. 87.

‡ *Bul. Scient. de St. Pétersb.*, t. x. No. 18, and Liebig's *Ann.*, Bd. xlv. p. 283.

§ $n = 1$ or 2 .

wise be transformed into a similar body, $C_{12} \left\{ \begin{smallmatrix} H_{5-n} \\ Cl_n \end{smallmatrix} \right\} NO_4$, and this body would require only to be treated with sulphuretted hydrogen to be changed into the desired compound.

Whilst occupied with the preparation of anthranilic acid, for the purpose of these experiments, another expedient offered itself, which, by changing completely the direction of my researches, led me quickly to the desired object.

It is well known that it is not necessary to employ pure anthranilic acid for the preparation of aniline, which may be obtained directly as a true product of oxidation by distilling indigo and hydrate of potash, as is shown in the following manner:—

We may here take a short review of the substances obtained from indigo by other oxidizing means. By the action of nitric acid there is formed as the first product of oxidation a body named isatine, which was discovered by Laurent and Erdmann about the same time. This compound contains the elements of indigo, together with 2 equivalents of oxygen,

Aniline being, as was already remarked, a product of oxidation of indigo, it was in the highest degree probable, not to say certain, that it could also be obtained from isatine by fusing the latter with hydrate of potash. This question remained to be decided by experiment.

ACTION OF HYDRATE OF POTASH IN FUSION ON ISATINE*.

On pouring a solution of caustic potash on isatine in a tubulated retort, its colour becomes dark red, almost amounting to black, which, according to Laurent, is owing to a trans-

* All the isatine employed in the following experiments was prepared from commercial indigo, according to the method of Laurent, with common nitric acid; a very considerable quantity is thus obtained. In its preparation care must be taken not to employ too large a quantity of nitric acid, otherwise there is formed the indigotic acid discovered by Buff (also called aniline, and nitrosalicylic acid), which is at once recognised by the yellow colour of its crystals and the blood-red reaction with perchloride of iron. Neither must the indigo be mixed with too much water. After each addition of nitric acid effervescence should take place, which must be allowed to finish before adding a fresh quantity. Should this effervescence not take place, and a large quantity of nitric acid be added gradually to the boiling mixture, a most powerful reaction takes place at a certain point of concen-

272 Dr. Hofmann on the *Metamorphoses of Indigo*.

itory combination of isatine with potash. By warming the potash-ley, a solution of the dark red crystals is made of the same colour, but so soon as the fluid comes to the boiling-point the colour changes to orange-yellow, and contains now isatin-ate of potash. At the beginning of the distillation pure water passes over, but at a certain concentration of the fluid, which can be hastened by the addition of pieces of solid hydrate of potash, a lively reaction takes place, and there distils over with the water a body in the form of oily drops, which possesses all the properties of aniline. During the operation, and particularly at the end, free hydrogen gas is evolved, and carbonate of potash remains in the retort. The following formula exhibits the decomposition:—

After this experiment, the preparation of the desired compounds was no longer a matter of difficulty. They must be obtained by the action of alkaline bases on chlorisatine and bichlorisatine.

The experiments about to be detailed will show how far this conclusion was correct, supported as it was by the complete analogy existing between isatine, chlorisatine and bromisatine.

ACTION OF FUSED HYDRATE OF POTASH ON CHLORISATINE.

On distilling chlorisatine* with a mixture of potash-ley and solid hydrate of potash, exactly the same phenomena present themselves as in the case of isatine, with the single difference, tration of the fluid, and the mass flows over the largest vessels. The portions remaining contain generally only indigotic acid.

Isatine may be purified very easily in the following manner:—The crude product, still containing a quantity of resinous matter, is dissolved in potash-ley, and then carefully decomposed by the addition of hydrochloric acid so long as there is formed a black or brown precipitate. Should a small filtered portion possess a pure yellow colour, or the precipitate arising from the further addition of hydrochloric acid be of a pure lively red, the whole fluid is then to be separated by filtration from the resin and completely decomposed by hydrochloric acid. After washing with water, isatine obtained in this way is chemically pure.

* For the preparation of large quantities of chlorisatine I have always employed isatine, from the fact that chlorine in its action on indigo produces a mixture of chlorisatine and bichlorisatine, which can with difficulty be separated. Isatine is therefore much more convenient for this purpose. The change can be very much hastened by suspending isatine in boiling water, and directing a stream of chlorine through the fluid under the direct influence of the sun's rays. The transition is instantly recognised by the orange-yellow colour assumed by the crystals. As already stated by Erdmann (*Journal für Prakt. Chem.*, Bd. xxii. S. 272), not a trace of bichlorisatine is formed in this reaction, a fact also confirmed by my experiments.

that the oily fluid which distils over with the water condenses into a white crystalline mass in the neck of the retort, or, if this is too hot, in the cooled receiver. If the distillation is carefully conducted to prevent any of the fluid spirting over, the product collected in the receiver *does not react alkaline* so long as there remains a considerable quantity of water in the retort. When, however, the substance in the retort becomes nearly dry, a considerable quantity of ammonia, together with hydrogen, begins to be evolved, and the upper part of the retort becomes covered with a blue matter, which is sometimes carried over with the watery vapour into the receiver; at the same time the oily drops which have distilled over, from being colourless, now become brown and no longer solidify. At this period the distillation must be interrupted.

The crystalline substance which collects in the receiver can be purified with the greatest ease, by being thrown on a filter and washed with distilled water till all trace of ammonia is removed. To obtain it chemically pure, it is to be dissolved in boiling alcohol, from which it crystallizes in regular octahedrons. From the analysis it will be seen that this compound is aniline, in which one equivalent of hydrogen is replaced by one equivalent of chlorine. In short, it presents all the chemical characters and properties of aniline, and is like it a *base*. It may hence be denominated "chloraniline." If we employ the very excellent nomenclature of Laurent, who designates aniline by the name amaphenese (phenamide), then must the new chlorinated base be called amachlophenese.

A. *Chloraniline (Amachlophenese)*.

a. *Composition*.

This substance was prepared and purified in the way above mentioned, and then dried in the air; in consequence of its containing chlorine, the combustion was made with chromate of lead.

I. 0.4495 grm. of substance gave 0.9210 grm. of carbonic acid and 0.1980 grm. of water.

II. 0.3220 grm. of substance gave 0.6670 grm. of carbonic acid and 0.1495 grm. of water.

III. 0.283 grm. of the substance well-mixed with powdered lime was placed in a tube, small pieces of lime added, and then submitted to a strong heat*. The residue, dissolved in

* Strong heat is necessary, as the substance is decomposed with difficulty. In a previous operation a small quantity distilled over undecomposed, which made the amount of chlorine too small.

0.3925 grm. of substance gave 0.400 grm. chloride of silver = 25.14 per cent. chlorine.

274 Dr. Hofmann on the *Metamorphoses of Indigo*.

nitric acid and precipitated by nitrate of silver, gave 0.315 grm. of chloride of silver.

IV. The determination of the nitrogen was made in an atmosphere of carbonic acid. 0.597 grm. of substance burned with peroxide of copper gave, at 334^{mm} barom. and 11° centigrade, 58. cub. cent. of nitrogen. These numbers correspond to the following per-centage:—

	I.	II.	III.	IV.
Carbon*	= 55.88	56.49		
Hydrogen	= 4.89	5.15		
Chlorine	=		27.45	
Nitrogen	=			11.38

These numbers may be expressed in the following formula,—

$C_{12} \left\{ \begin{smallmatrix} H_6 \\ Cl \end{smallmatrix} \right\} N$, as is shown by comparison of the numbers calculated and found.

	Theory.	Per cent.	Mean of experiment.
12 Carbon	= 900.00	56.43	56.18
6 Hydrogen	= 75.00	4.70	5.02
1 Chlorine	= 442.65	27.75	27.45
1 Nitrogen	= 177.04	11.10	11.28
1 æq. Chloraniline	= 1594.69	100.00	99.95

To control this formula, I prepared the platinum double salt, which crystallized beautifully, and, after drying at the temperature of the air, analysed it. 0.5095 grm. of this salt, after combustion, left 0.1495 grm. = 29.34 per cent. of platinum; the atomic weight found from this = 1626.85; theoretical atomic weight = 1594.69. The agreement between the two is sufficiently near.

By adopting the formula $C_{12} \left\{ \begin{smallmatrix} H_6 \\ Cl \end{smallmatrix} \right\} N$, which is completely established by the analyses of the different salts and the products of decomposition of the base, the formation of this body can be explained in the most satisfactory manner. It is, as was to be expected, completely analogous to the formation of aniline from isatine, as is shown by the following formulæ:—

I shall return afterwards to the origin of the ammonia in the last stage of the preparation.

b. Properties of Chloraniline.

I have already stated that this base is soluble in alcohol,

* Carbon = 75. Hydrogen = 12.5.

from which it crystallizes on cooling or by evaporation in regular octahedrons, in which the axes, as in the crystals of alum, have the planes of the cubes developed in a very high degree. I have obtained completely formed crystals, the axes of which were about a centimetre in length, and could be therefore submitted to the most exact crystallographic examination; they are not altered by exposure to the air. By rapidly cooling a boiling alcoholic solution of this base, it is deposited in the form of small, regular octahedrons, which present the most striking resemblance to codeine. The facility with which this body crystallizes is indeed remarkable; its solution yields by evaporation regular crystals even to the last drop.

This base is also extremely soluble in æther, pyro-acetic spirit, acetone, bisulphuret of carbon, fatty and æthereal oils. Water dissolves it but sparingly. By rapid cooling the boiling saturated solution becomes milky; but by proceeding slowly the base is deposited in well-defined small octahedrons, possessing the lustre of the diamond. By agitation with æther the base is withdrawn from the aqueous solution. Its odour is pleasant, somewhat like wine; its taste aromatic and burning. In both respects it cannot absolutely be distinguished from aniline. The crystals melt by heat. On making the experiment with a considerable quantity, the whole mass fused at a temperature of 64° to 65° cent. into a yellow oily liquid, which solidified on cooling into a mass of large octahedrons, the thermometer sinking at the same time to 57° cent. This base is in the highest degree volatile. The alcoholic solution cannot be evaporated without considerable loss. Even at common temperatures the crystals volatilize, as may be seen by the white vapours which arise on bringing near them a glass rod moistened with hydrochloric acid. With water the base can easily be distilled. In an experiment to distil it alone, made with a small quantity, I always obtained, besides the oily drops, the blue product of decomposition which I have already stated is formed in the preparation of the base. This decomposition prevents the determination of the boiling-point, which at all events lies above 200° cent. The vapour of the base burns with a brilliant smoky flame, possessing the green-coloured border peculiar to organic compounds containing chlorine.

It is heavier than water, and neither alone nor in solution does it exhibit the least reaction on turmeric or reddened litmus paper. Dahlia paper is coloured of a feeble green.

From what has been stated, it appears that chloraniline almost completely corresponds in its physical properties to aniline. The chief difference is that aniline is fluid at common temperatures, whilst the chlorinated compound is solid.

276 Dr. Hofmann on the *Metamorphoses of Indigo*.

In their relation to other bodies, both compounds also agree, but to a more limited extent. The intense yellow colour given to pine-wood and the pith of the elder tree by acid solutions of aniline, is also produced by the salts of the chlorinated compound. On the other hand, the characteristic violet colour communicated to aniline by chloride of lime, is not exhibited by the compound derived from it; a solution of this reagent by mixture with this body assuming only a slight shade of violet. The solution of the salts takes the same colour, which however rapidly passes into orange. Neither is a cold or hot watery solution of the base nor of its salts altered by chromic acid, whilst aniline under the same circumstances gives rise to dark or greenish-blue products. On adding chromic acid to the crystals of the chlorinated base, they become brown and resinify. A mixture of these crystals with solid chromic acid inflames at the fusing-point of the base.

With regard to its relation to other reagents, I have to remark the following:—Peroxide of iron is not precipitated by the watery or alcoholic solution of the base. In both cases the fluid becomes green, from a partial reduction of the per-salt of iron. By employing a watery solution of the base or crystals of it, a violet product of oxidation separates at the boiling-point, which is soluble in alcohol. No change is produced in protosalts of iron, nor in sulphates of alumina or of zinc, even by boiling them with the crystals. These oxides, however, are precipitated by aniline, from which it is evident that by the entrance of chlorine into its composition, its basic properties are somewhat enfeebled. Sulphate of copper is not precipitated by a watery solution of the base, but on adding some of its crystals to a boiling copper solution, the latter is immediately decolorized, and then deposits a mass of crystals of a bronze colour, which are insoluble in water, but are partially dissolved in boiling alcohol, from which on cooling they crystallize in the form of scales. It appears to be a double salt of sulphate of copper and of the chlorinated base. Similar double salts are produced with the perchlorides of mercury, platinum and palladium; the first of these being white, the latter two of a splendid orange-yellow colour. The precipitate from a gold solution is reddish brown. Tincture of galls is not changed by a cold solution of the base, but on adding a hot saturated solution, a yellow flocky precipitate is produced on cooling. Other chemical reagents are not affected by its watery solution.

c. Compounds of Chloraniline.

The extraordinary facility of crystallizing which distin-

guishes the chlorinated base are found in nearly all its compounds with acids; most of them are precipitated as a crystalline mass by mixing its alcoholic solution with the respective acids. By recrystallization from boiling water or alcohol they are obtained quite pure; with the exception of the platinum and palladium double salts they are white, but the larger crystals have generally a shade of yellow. An excess of acid imparts to them a violet tint. An elevation of temperature is observed in the formation of these compounds, &c.; they possess the true character of salts by their capability of undergoing double decomposition. As this base has no alkaline reaction, all its salts, as a consequence, possess acid properties. A large excess of the base can be heated to fusion under dilute hydrochloric acid without removing the acid properties of the supernatant fluid.

The salts are decomposed with the greatest ease by the caustic and carbonated alkalis; in the latter case with evolution of the carbonic acid, which does not unite with the base. The base itself separates in the form of a crystalline mass. The same decomposition is also produced by hydrochlorate of ammonia in solution. By heating it, however, in a tube with hydrochlorate of ammonia, evolution of ammonia takes place, and the hydrochlorate of the base is deposited on the cool portion of the tube.

Its capacity of saturation is the same as that of aniline, although the atom of the latter is lower than that of the former by the difference of the equivalents of chlorine and hydrogen ($442.65 - 12.50 = 430.15$).

The constitution of the salts in no respect differs from those of ammonia. They unite directly with the hydracids, and with the oxacids by the addition of an equivalent of water.

The alcoholic solution of chloraniline forms, by the addition of a few drops of sulphuric acid, a white crystalline mass, which by re-solution in boiling water separates on cooling as a confused mass of tabular crystals. From boiling alcohol, in which the salt is less soluble, it crystallizes in stellated tufts of fine silvery needles. Their crystalline form cannot however be determined. Even by slow evaporation of the alcoholic, as well as the watery solution, over sulphuric acid, I was unable to obtain large crystals. The salt is not volatile. By heating, a portion of the base escapes unchanged, while the remainder becomes black and evolves sulphurous acid.

Only one combustion of this salt was made. 0.3445 grm.

278 Dr. Hofmann on the *Metamorphoses of Indigo*.

gave 0.5290 grm. of carbonic acid and 0.1365 grm. of water. These numbers correspond in the 100 parts to

Carbon . . . = 41.87

Hydrogen . . . = 4.40

The formula is $\text{SO}_3, \text{C}_{12} \left\{ \begin{smallmatrix} \text{H}_6 \\ \text{Cl} \end{smallmatrix} \right\} \text{N} + \text{HO}$, which gives

Carbon . . . = 40.75

Hydrogen . . . = 3.96

The excess of carbon arises from the formation of a small quantity of deutoxide of nitrogen, which almost always takes place in the combustion of such bodies, if a very considerable quantity of copper turnings is not placed at the fore part of the combustion tube. I did not think it necessary to repeat this analysis, as it was only intended to give a view of the constitution of the salt.

Binoxalate of Chloraniline, $2\text{C}_2\text{O}_3, \text{C}_{12} \left\{ \begin{smallmatrix} \text{H}_6 \\ \text{Cl} \end{smallmatrix} \right\} \text{N} + \text{HO} + 2 \text{ aq.}$

By dissolving crystals of chloraniline in a warm watery solution of oxalic acid, a salt separates on cooling, which by re-crystallization from hot water is obtained in long needles like saltpetre. These consist of closely agglomerated prisms, and hence could not be used for the determination of the crystalline form. The salt is difficultly soluble in cold water and alcohol. It is without smell, but possesses a sweetish burning taste. Its solution becomes coloured on exposure to the air, and deposits gradually a red powder. The following results were obtained on burning this compound with chromate of lead:—0.4475 grm. gave 0.6990 grm. of carbonic acid and 0.171 grm. of water, or in the 100 parts,

Carbon . . . = 42.59

Hydrogen . . . = 4.24

These numbers give the following formula:—

$2 \text{C}_2 \text{O}_3, \text{C}_{12} \left\{ \begin{smallmatrix} \text{H}_6 \\ \text{Cl} \end{smallmatrix} \right\} \text{N} + \text{HO} + 2 \text{ aq.}$

	Theory.	Found.
16 equiv. of Carbon . .	1200.00	42.59
9 ... Hydrogen . .	112.50	4.24
1 ... Chlorine . .	442.65	
1 ... Nitrogen . .	177.04	
9 ... Oxygen . .	900.00	
	2832.19	

To control this formula I determined the amount of oxalic acid in the salt. 0.339 grm. of the salt, saturated with am-

monia and precipitated by chloride of calcium, gave, after heating to redness, 0.153 grm. of carbonate of lime, which corresponds to 32.18 per cent. of anhydrous oxalic acid.

	Theory.		Found.
2 equiv. of Oxalic acid =	900.00	31.77	32.18
1 ... Base . . =	1594.69	56.30	
3 ... Water . . =	337.50	11.93	
	2832.19	100.00	

The above salt corresponds in its constitution to the bin-oxalate of ammonia and to Zinin's binoxalate of naphthalidan. As a neutral oxalate of aniline is known, I thought I might obtain the neutral salt of the chlorinated base by mixing its watery solution with oxalic acid in such a way as to leave the former in great excess. From this mixture, on cooling, separated needle-form crystals, which were washed and recrystallized. The combustion with chromate of lead gave from 0.4215 grm., dried at the temperature of the air, 0.6565 grm. of carbonic acid and 0.1490 grm. of water, corresponding in the 100 parts to

Carbon 42.69

Hydrogen 3.92

hence proving that even under the conditions above-mentioned an acid salt had been formed.

An acid oxalate of aniline has not as yet been analysed. I endeavoured to form such a salt by saturating aniline with a large excess of oxalic acid. The precipitate formed was washed and frequently recrystallized from water. The needles obtained in this way possessed great similarity to the acid salt of the chlorinated base; they were, however, neutral oxalate of aniline, as was proved by the combustion. 0.3660 grm. of the salt gave 0.8188 grm. of carbonic acid and 0.2088 grm. of water. In 100 parts,

Carbon 61.01

Hydrogen 6.33

The formula is $C_2O_3, C_{12}H_7N + HO$, which gives

Carbon 60.79

Hydrogen 5.79

Nitrate of chloraniline is obtained by simply heating the base in dilute nitric acid. On cooling, the fluid becomes filled with tabular crystals, which generally possess a reddish tint. The salt is tolerably soluble in both alcohol and water. By heat it fuses into a dark mass, which forms with alcohol a beautiful rich blue solution, from which the nitrate, partly unchanged, again separates. I could not sublime this compound.

Phosphate of Chloraniline.

A solution of the base in alcohol forms, with phosphoric acid, a thick mass of crystalline plates, which are tolerably soluble in alcohol and water. I have not made any further investigation of this salt.

Hydrochlorate of Chloraniline, $\text{Cl H, C}_{12}\left\{\begin{smallmatrix} \text{H}_6 \\ \text{Cl} \end{smallmatrix}\right\}\text{N}$.

Forms large, colourless, transparent crystals, which are obtained on cooling from a hot saturated solution of the base in hydrochloric acid. By redissolving in water and slowly evaporating the dilute solution over sulphuric acid, large well-formed crystals are produced. In describing the corresponding bromine compound I shall speak more of their crystalline form. They remain unchanged on exposure to the air, but become white and opaque by the application of heat. If the heat be carefully applied they can be sublimed in a tube like sal-ammoniac; by sudden elevation of the temperature, however, the salt is decomposed with evolution of a violet-blue vapour.

The analysis of the crystals, dried at the temperature of the air, gave the following results:—0·3155 grm. of the salt precipitated with nitrate of silver gave 0·271 grm. of chloride of silver, corresponding to 22·10 per cent. of hydrochloric acid, which leads to the formula $\text{Cl H, C}_{12}\left\{\begin{smallmatrix} \text{H}_6 \\ \text{Cl} \end{smallmatrix}\right\}\text{N}$.

	Theory.		Experiment.
1 eq. Chloraniline . . .	1594·69	77·80	77·90
1 eq. Hydrochloric acid =	455·15	22·20	22·10
1 eq. Hydrochlorate of chloraniline . . . }	2049·84	100·	100·

Chloraniline and Bichloride of Platinum.

A solution of chloraniline in hydrochloric acid is precipitated of an orange-yellow colour by bichloride of platinum. If the two solutions are mixed hot, the whole fluid on cooling becomes a mass of crystalline plates. This double salt is very soluble in water, spirits of wine, and even in a mixture of alcohol and æther. To obtain it pure it is to be washed with cold water till the fluid, which continues to possess an evident acid reaction, passes colourless. On exposing the moist salt to the light, it becomes of a violet colour on the surface, which arises probably from the oxidizing ac-

tion of the bichloride of platinum by the presence of water. Evaporated over sulphuric acid this salt forms little rounded lumps, which exhibit no facets. On burning with chromate of lead the following result was obtained:—

0·463 grm. of the platinum double salt gave 0·374 grm. of carbonic acid and 0·096 grm. of water; corresponding in the 100 parts to

Carbon . . .	22·03
Hydrogen . . .	2·30

These numbers, with the determination of the platinum already mentioned, give the following formula:—

		Theory.	Experiment.
12 equiv. Carbon . .	= 900·00	21·53	22·03
7 ... Hydrogen . .	= 87·50	2·09	2·30
4 ... Chlorine . .	= 1770·61	42·47	
1 ... Nitrogen . .	= 177·04	4·24	
1 .. Platinum . .	= 1233·50	29·46	29·34
1 eq. of the double salt =		4168·65	

Bichloride of Mercury and Chloraniline.

This salt can be obtained in beautiful fine needles by pouring an alcoholic solution of the base into a hot solution of corrosive sublimate. At first the fluid remains clear, but after a few moments begins to get turbid, and gradually thickens completely into a mass of needle-form crystals of the double salt. I have not investigated other salts of the base. I may, however, mention a very beautiful double salt formed with chloride of zinc: by the mixture of the two solutions the fluid remains at first clear, but after a short time becomes a mass of silvery crystals.

d. Products of the Decomposition of Chloraniline.

I have not as yet so fully studied the products of the decomposition of this base as they deserve. Indeed it appears to suffer in contact with other bodies the same changes as aniline. The presence of the chlorine seems to have no influence in the processes of transformation, but passes over into the new products just as the hydrogen of aniline which it has replaced. I intend to investigate this subject more fully, and shall mention here only those phenomena which came under my observation during the course of the present inquiry.

Action of the Oxygenated Compounds of Chlorine on Chloraniline.

On adding crystals of this substance to a mixture of chlo-

282 Dr. Hofmann on the *Metamorphoses of Indigo*.

rate of potash and hydrochloric acid, the fluid at first becomes violet-red and then gradually turbid and brown. The action is much hastened by the addition of alcohol, by which at the same time, however, acetic æther is formed. By long-continued action the fluid becomes again colourless, and a yellow crystalline matter is obtained, which can be easily purified by washing with alcohol and æther, in which it is but little soluble.

This substance crystallizes from boiling alcohol on cooling in small yellow plates. By slowly heating it sublimes without residue in the form of beautiful glittering scales of a golden colour. Potash forms with it a blood-red solution, from which, after some time, ruby-red prisms separate, which become of a vermilion colour by moistening with hydrochloric acid, and after removal of the acid dissolve in pure water with a beautiful violet colour. All these phænomena characterize in an undoubted manner the chloranil discovered by Erdmann in his investigations on indigo, a substance which, as I proved* a few months ago, is formed also in many other processes.

If the action of the oxidizing mixture on the chloraniline is not allowed to go so far, the chloranil is obtained mixed with a viscid matter, which is very soluble in alcohol and æther. On evaporating off the æther and submitting the resinous residue to distillation, oily drops pass over and crystallize in the neck of the retort. They possess the characteristic smell and peculiar reactions which distinguish the chlorophenissic or chlorophenussic acid of Laurent, namely the forming a violet precipitate with sulphate of copper, and a citron yellow with nitrate of silver.

The formation of all these bodies is easily explained. The nitrogen with a portion of the hydrogen forms ammonia, the presence of which can be proved in the mother-liquor. The remaining hydrogen is entirely or partially replaced by chlorine, chlorine and oxygen being called into action in the mixture of hydrochloric acid and chlorate of potash, whilst at the same time oxygen enters into the compound.

The following formulæ show the reactions:—

Chloraniline.

Chloranil.

Chloraniline.

Chlorophenissic acid.

Chloraniline.

Chlorophenussic acid.

* Mem. Chem. Soc. vol. ii. p. 227.

Chloraniline thus gives, under the same circumstances, as was to be expected, the same products of decomposition as aniline.

Action of Chlorine on Chloraniline.

At the commencement of this memoir are given the facts observed by the action of chlorine on aniline. The chlorinated base suffers precisely the same decompositions. There are formed chlorophenissic acid and a neutral body, the latter being trichloraniline, $C_{12}\left\{\begin{smallmatrix} H_4 \\ Cl_3 \end{smallmatrix}\right\}N$. I shall return immediately to its preparation and its properties.

Action of Bromine on Chloraniline.

By mixing aniline with bromine, heat and hydrobromic acid are disengaged, and there is formed Fritzsche's bromaniloid (tribromaniline), $C_{12}\left\{\begin{smallmatrix} H_4 \\ Br_3 \end{smallmatrix}\right\}N$. The chlorinated base suffers the same decomposition with bromine. The product differs from the foregoing only in containing chlorine. It has the following composition, as we shall see afterwards:—

Action of Nitric Acid on Chloraniline.

The decomposition produced in the chlorinated base by nitric acid I have unfortunately as yet but incompletely studied, although this point would have been of particular interest to have cleared up satisfactorily.

By the action of nitric acid aniline is transformed into carbazotic acid. It is in the highest degree probable that by the action of this oxidizing agent on chloraniline picric acid is formed, in which 1 equiv. of hydrogen is replaced by 1 of

chlorine, having the formula $C_{12}\left\{\begin{smallmatrix} H \\ Cl \\ 3NO_4 \end{smallmatrix}\right\}O + HO$. By add-

ing concentrated nitric acid to the chlorinated base, a lively reaction takes place, the fluid remains for some time boiling without the application of external heat, evolves nitrous acid, and becomes dark red, and finally black and opaque. By continued action it becomes again transparent, and by allowing the scarlet red fluid to cool there sometimes separate golden yellow needles, which are very similar to the nitropicric acid. No trace of chlorine can be then detected in the fluid by nitrate of silver.

I made a great number of experiments to discover under what conditions this body was formed, but as yet I have not been able to produce it at will. In most cases I obtained instead a resinous body, which was precipitated in the form of yellow flakes from the nitric acid by addition of water, and which possessed the same property as nitropicric acid of tinging the skin. This substance is soluble in alcohol and æther, but cannot be obtained from the solution in a crystalline form. It is also soluble in the alkalies and ammonia, and is again precipitated by acids. By boiling the ammoniacal solution till the excess of ammonia is removed, and then adding nitrate of silver, a reddish-yellow precipitate is formed, which I was able to obtain only on one occasion in a crystalline form. My substance was, however, all expended ere I could discover a good method of preparation. Further experiments are necessary to decide the correctness of the forementioned hypothesis.

Action of Anhydrous Baryta and Lime on Chloraniline.

Though the examples are numerous in which the hydrogen of organic bodies has been replaced by chlorine, yet chemists have seldom been able to expel, without complete disorganization of the body, the assumed chlorine and refix the hydrogen in its old position. Indeed I know of no other instance than that of the regeneration of acetic acid from the chloracetic, performed by Melsens, by the employment of potassium amalgam.

From chloraniline can likewise be reproduced. If a few crystals be placed in the end of a combustion-tube and lime in small pieces be laid before it, on heating the lime to a low red heat, there distils over a yellow oil which no longer becomes crystalline, and by all its reactions is at once recognised as aniline. At the same time a considerable quantity of ammonia is evolved, and there remains in the tube chloride of calcium and a large quantity of carbonaceous matter.

The regeneration of aniline is, as must be at once seen, essentially different from that of the acetic acid. In the reproduction of acetic acid from the chloracetic the hydrogen assumed is derived from the water present, its oxygen serving to oxidize the potassium; in the case of aniline the requisite hydrogen is furnished by that substance itself, which must consequently be partly decomposed. One equivalent of the chlorinated base contains just sufficient hydrogen to convert its nitrogen into ammonia, its own chlorine and that of another equivalent of base into hydrochloric acid, and finally, to furnish the required equivalent of hydrogen to the now regene-

rated aniline. Its carbon must, therefore, be completely separated. The following formula exhibits this change:—

This decomposition gives the key to some phenomena of which I have already made mention in the preparation of chloraniline.

I mentioned that in the last stage of the distillation, so soon as the mass in the retort commences to become dry, evolution of ammonia takes place, and aniline at the same time distils over. This reaction evidently depends on a transformation similar to that just mentioned. The vapours of the chlorinated base which deposit on the cooler parts of the apparatus meet with hot potash on the sides of the retort, and are decomposed into aniline, ammonia, and hydrochloric acid.

By carefully mixing a small portion of very pure chlorisatine with caustic baryta and slowly heating, a product of distillation was obtained which did not exhibit the slightest alkaline reaction, whilst, in the heated residue, not a trace of chlorine could be detected. All the nitrogen and chlorine of the chlorisatine had consequently distilled over in the form of chloraniline.

Action of Potassium on Chloraniline.

The decomposition experienced by the chlorinated base when its vapour is passed over fused potassium offers no great peculiarity. The potassium becomes incandescent and is converted into chloride and cyanide. A large quantity of carbon is also deposited.

ACTION OF THE FUSED HYDRATE OF POTASH ON DICHLORISATINE.

B. Dichloraniline (Amachlophenise).

Erdmann has proved by direct experiment that chlorisatine cannot be converted into dichlorisatine by the further action of chlorine on this substance suspended in water. I have had frequent opportunities of convincing myself likewise of this fact. If an alcoholic solution be employed the decomposition proceeds too far, and products of oxidation are obtained, viz. chloranil, chlorophenussic acid, &c., which no longer belong to the isatine series.

I endeavoured to prepare dichlorisatine by dissolving isatine or chlorisatine in potash and passing a stream of chlorine

gas through the solution of isatinate or chlorisatinate of potash. The result was however unfavourable. No dichlorisatine was formed, but in its stead a tarry matter, which floated on the surface of the fluid; it was insoluble in water but soluble in alcohol. I was equally unsuccessful in dissolving chlorisatine in nitric acid and adding to the solution a few drops of hydrochloric acid. A violent reaction ensued, and the decomposition had evidently proceeded too far. There remained, therefore, only to fall back upon the method employed by Erdmann to prepare this substance, and of which Laurent had also made use in his investigation. It consists in treating indigo directly with chlorine. In this process, under every circumstance, there is formed a mixture of chlorisatine and dichlorisatine, the quantity of the latter, according to Erdmann, greatly preponderating. Chlorisatine and dichlorisatine can only be separated from each other by crystallization with extreme difficulty. The amount I had obtained was too small to think of trying to separate them in this way; I therefore at once submitted the mixture with hydrate of potash to distillation.

The distilled product contained, besides chloraniline, another basic substance, collecting on the surface of the fluid, which crystallized in long prisms. This substance was manifestly nothing but dichlorisatine, $C_{12}\left\{\begin{smallmatrix} H_5 \\ Cl_2 \end{smallmatrix}\right\}N$. The crystals which could be picked out of the fluid unfortunately were not sufficient in amount for a combustion. As I have, however, more completely studied the corresponding bromine compound, which is much more easily prepared, I considered it useless to occupy myself longer with this substance.

C. *Trichloraniline* (*Amachlophenose*). $C_{12}\left\{\begin{smallmatrix} H_4 \\ Cl_3 \end{smallmatrix}\right\}N$.

Isatine, in which 3 equivalents of hydrogen are replaced by three of chlorine, is as yet not known. The preparation of trichloraniline could not hence be made by persevering in the method hitherto used. It is however procured, as above mentioned, by the direct action of chlorine on aniline or the chlorinated base.

By submitting to distillation with hydrate of potash the crude product of the action of chlorine on these two bodies, which contains a mixture of chlorophenissic acid and trichloraniline, the first remains in the retort in combination with potash, while the latter passes over into the receiver with the watery vapour, and collects on the surface of the liquid in long needles. As this substance is very volatile, a cooling apparatus must always be employed in this distillation.

Trichloraniline is very little soluble in water, but dissolves readily in alcohol and æther. The solution has a neutral reaction. It does not unite with bases or acids, and can be distilled unchanged from water containing either acid or alkali.

This substance is obtained only in small quantities. My whole amount, after the qualitative determination of chlorine and nitrogen, was just sufficient for one analysis, which unfortunately did not turn out very good, but could not be repeated from the fact already mentioned. By burning with chromate of lead the following results were obtained:—

0.3020 grm. of the substance gave 0.4170 grm. of carbonic acid, 0.0665 grm. of water. In the 100 parts—

Carbon	. . .	37.65
Hydrogen	. . .	2.44

The formula is $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Cl_3 \end{smallmatrix} \right\} N$. The theoretical constitution is

12 equiv. Carbon	=	900.00	36.66
4 ... Hydrogen	=	50.00	2.03
3 ... Chlorine	=	1327.95	54.09
1 ... Nitrogen	=	177.04	7.22
		<hr/> 2454.99	<hr/> 100.

It may perhaps appear bold to give an opinion as to the constitution of this body from a single determination of its carbon and hydrogen, which, besides, does not agree very well with the theory. When however we consider the complete analogy in the mode of formation of tribromaniline and chlorodibromaniline, to which I shall afterwards return, and the exact resemblance in the properties of these bodies, less doubt may perhaps be entertained.

It appeared to me also to be worth the trouble of endeavouring to form a base which contained bromine as well as chlorine. Such a body could with ease be obtained, were it possible to form a chlorobromisatine, $C_{16} \left\{ \begin{smallmatrix} H_3 \\ Cl \\ Br \end{smallmatrix} \right\} NO_4$. Distilled

with hydrate of potash, this compound would yield chlorobrominated aniline, $C_{12} \left\{ \begin{smallmatrix} H_5 \\ Cl \\ Br \end{smallmatrix} \right\} N$. For this purpose, I poured

on chlorisatine in a retort an excess of bromine, allowed the whole to remain for twelve hours, and then heated it in a water-bath to the boiling-point, until the excess of bromine was distilled off. The red crystals were separated by filtration, washed and crystallized from hot alcohol.

288 Dr. Hofmann on the *Metamorphoses of Indigo*.

The prismatic crystals thus obtained produced on burning with chromate of lead the following result:—

0.2955 grm. gave 0.5697 grm. of carbonic acid and 0.0695 grm. of water; corresponding in the 100 parts to

Carbon . . . 52.57

Hydrogen . . . 2.61

This substance was consequently nothing but pure undecomposed chlorisatine, which contains in 100 parts—

Carbon . . . 52.88

Hydrogen . . . 2.25

This compound, $C_{16} \left\{ \begin{smallmatrix} H_3 \\ Cl \\ Br \end{smallmatrix} \right\} NO_4$, would have contained

Carbon . . . 36.90

Hydrogen . . . 1.15

The small quantity of hydrobromic acid observed in this action of bromine on chlorisatine may have arisen from a small admixture of isatine, which would be converted into bromisatine. By continued action of bromine in sunshine, perhaps another result might be obtained.

D. *Chlorodibromaniline* (*Amachlobrophenose*). $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Cl \\ Br_2 \end{smallmatrix} \right\} N$.

It has been already stated that aniline is decomposed with facility by bromine. On adding bromine water to the solution of a salt of chloraniline, a white precipitate takes place, which dissolves in boiling alcohol, producing a slight violet colour, and crystallizes on cooling in needles. The same compound can be obtained by the direct action of bromine on chloraniline. On adding bromine to the crystals of the latter, a very violent reaction takes place, with great elevation of temperature and evolution of hydrobromic acid, the mixture at the same time assuming a violet colour. Bromine is to be added till the mass on being fused no longer absorbs any more. The crystalline product is then to be allowed to cool, and well-washed till all trace of hydrobromic acid is removed. By recrystallization from alcohol, white crystals are obtained, which have generally a shade of red.

Fritzsche, as is known, has discovered that by the action of bromine on aniline there is formed a body, $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Br_3 \end{smallmatrix} \right\} N$, which he called bromaniloid. From this decomposition we can already foresee the composition of the product which I obtained by the action of bromine on the chlorinated base. This must stand in the same relation to the bromaniloid that

the chlorinated base does to aniline, and consequently would be expressed by the formula $C_{12} \left\{ \begin{matrix} H_4 \\ Cl \\ Br_2 \end{matrix} \right\} N$.

This conclusion is completely confirmed by the analysis.

The combustion with chromate of lead gave the following results:—

0·520 grm. crystals, dried at the temperature of the air, gave 0·485 grm. of carbonic acid and 0·070 grm. of water; corresponding in the 100 parts to

Carbon . . . 25·43

Hydrogen . . . 1·52

which will give the calculated composition,—

		Theory.		Experiment.
12 equiv. Carbon	. . .	= 900·00	25·52	25·43
4 ... Hydrogen	. . .	= 50·00	1·41	1·52
1 ... Chlorine	. . .	= 442·65		
2 ... Bromine	. . .	= 1956·61		
1 ... Nitrogen	. . .	= 177·04		
1 ... Chlorodibromaniline		= 3526·30		

The formula of this compound is $C_{12} \left\{ \begin{matrix} H_4 \\ Br_3 \end{matrix} \right\} N$, and it contains

Carbon = 22·15

Hydrogen = 1·22

This body is completely insoluble in water, but soluble in alcohol and æther. It melts under water into a brown oily fluid, which can be distilled over with the vapour of water; it crystallizes in shining needles on the sides of the receiver. Chlorodibromaniline, like the trichloraniline, no longer possesses basic properties. It is soluble in boiling hydrochloric acid, out of which however the greater part again recrystallizes unchanged on cooling. The portion soluble in hydrochloric acid at the ordinary temperature is precipitated by the addition of water. Strong sulphuric acid likewise forms with it a solution of a violet colour, from which it is also precipitated by the addition of water. Neither potash nor ammonia decomposes this substance, which by heat is slightly soluble in these fluids without the least change. It does not combine with bichloride of platinum or mercury, or with oxide of lead. Concentrated nitric acid decomposes the chlorodibromaniline.

ACTION OF FUSED HYDRATE OF POTASH ON BROMISATINE.

It was evidently to be expected that the brominated isatine would yield the same results as the chlorisatine. This was

290 Dr. Hofmann on the *Metamorphoses of Indigo*.

confirmed by experiment. Bromisatine has been as yet but little studied. Erdmann* obtained it in very small quantities by the direct action of bromine on indigo. Laurent did not prepare this substance; by the action of bromine on isatine he obtained immediately dibromisatine (bromisatinese). The first compound can however easily be formed by employing a solution of bromine in water instead of anhydrous bromine. In two experiments I obtained bromisatine alone, as is shown by the following analysis. The compound is dissolved out by boiling spirits of wine, washed with water to remove all trace of hydrobromic acid, and recrystallized in boiling alcohol, from which it separates in shining prisms

The following result was obtained on combustion with chromate of lead:—

I. 0·3270 grm. of bromisatine gave 0·5090 grm. of carbonic acid and 0·0625 grm. of water.

II. 0·3955 grm. of bromisatine gave 0·6165 grm. of carbonic acid and 0·0750 grm. of water.

These numbers give the following per-centages, which are placed in apposition with the calculated quantities:—

		Theory.		Experiment.	
				I.	II.
16 equiv. Carbon	. =	1200·0	42·41	42·45	42·51
4 ... Hydrogen	=	50·0	1·78	2·12	2·10
1 ... Bromine	. =	978·31			
1 ... Nitrogen	. =	177·04			
4 ... Oxygen	. =	400·00			
1 ... Bromisatine	=	2805·35			

The properties of this body, which I obtained in large quantities, agree completely with those of chlorisatine, to which on this account I refer in the memoirs of Erdmann and Laurent.

On submitting bromisatine to distillation with fused hydrate of potash, exactly the same phenomena are observed as those I have already described in the same process with chlorisatine, and there distils over a new base containing bromine.

E. *Bromaniline (Amabrophene)*.

a. *Composition*.

The purification of the crude product of distillation is made with the same ease as in the case of the corresponding chlorine compound. The analogy in the mode of formation of the two left no uncertainty as to the composition of bromani-

* *Journal für Prakt. Chem.*, Bd. xix, S. 358.

line. To banish all doubt, however, I determined the carbon and hydrogen.

The following results were obtained on combustion with chromate of lead:—

0·4152 grm. of the brominated base gave 0·6463 grm. of carbonic acid and 0·1405 grm. of water. The corresponding numbers in the 100 parts found and calculated are as follows:—

12 equiv. Carbon	. =	900·00	42·24	42·45
6 ... Hydrogen	=	75·00	3·52	3·75
1 ... Bromine	. =	978·31		
1 ... Nitrogen	. =	177·04		
1 ... Bromaniline	=	2130·35		

The formula is $C_{12} \left\{ \begin{smallmatrix} H_6 \\ Br \end{smallmatrix} \right\} N$. To control this formula the platinum double salt was prepared and analysed: 0·462 grm. gave 0·161 grm. = 26·19 per cent of platinum.

Atomic weight calculated from this . . . 2125·80

Theoretical atomic weight 2130·35

This agreement is sufficiently close.

b. Properties of Bromaniline.

The bromine base resembles in so high a degree the chlorine, that I shall have little to say on this point. It crystallizes also with the same facility in large, colourless, regular octahedrons, which in appearance can be as little distinguished from the chlorine base as the bromide from the chloride of potassium. The same similarity extends to its smell, taste and other properties. Its point of fusion, however, lies somewhat lower than that of the chlorine compound. At 50° cent. it melts to a violet oily liquid. On solidifying, the thermometer descends to 46° cent.

The salts of this base, like those of aniline and chloraniline, impart a yellow colour to pine-wood, and its watery solution communicates to chloride of lime a violet tint, much weaker than that caused by aniline, but, on the other hand, much stronger than that produced by chloraniline.

c. Compounds of Bromisatine.

What I have said with regard to the formation and preparation of the compounds of the chlorine base applies for the most part to the salts of the corresponding bromine base. I have only investigated some of these fully.

Oxalate of Bromaniline. $C_2 O_3, C_{12} \left\{ \begin{smallmatrix} H_6 \\ Br \end{smallmatrix} \right\} N, HO.$

On adding a watery solution of oxalic acid to this base

292 Dr. Hofmann on the *Metamorphoses of Indigo*.

dissolved in spirits of wine, a white crystalline precipitate is formed. This was separated by filtration, and recrystallized from boiling water. The crystals formed on cooling were indistinct in form, and with difficulty soluble in alcohol and water; insoluble in æther. The combustion of a portion dried at the ordinary temperature gave the following results:—

0.5635 grm. of the oxalate gave 0.8045 grm. of carbonic acid and 0.1695 grm. of water. These numbers correspond to the formula $C_2 O_3, C_{12} \left\{ \begin{smallmatrix} H_6 \\ Br \end{smallmatrix} \right\} N + HO$, as is seen by a comparison of the theoretical and experimental numbers.

	Theory.	Experiment.
14 equiv. Carbon .	= 1050.0	38.99
7 ... Hydrogen .	= 87.50	3.24
1 ... Bromine .	= 978.31	3.34
1 ... Nitrogen .	= 177.04	
4 ... Oxygen .	= 400.00	
1 ... Oxalate of } Bromaniline }	= 2692.85	

So that the brominated base forms, like aniline, the neutral oxalate under the same circumstances in which the acid salt of chloraniline is obtained.

Hydrochlorate of Bromaniline. $Cl H, C_{12} \left\{ \begin{smallmatrix} H_6 \\ Br \end{smallmatrix} \right\} N$.

This salt, which is obtained directly by dissolving bromaniline in hydrochloric acid, crystallizes on cooling from its hot saturated solution in a radiating filamentous mass. By slow evaporation of the solution over sulphuric acid, large well-formed crystals can be procured.

According to the determination of Dr. T. Müller, these crystals belong to the monoclinometric system (system hemiorthotype of Mohs).

The angle which is formed by the horizontal axis b and a is $=90^\circ$. The axis c forms with a a right, and with b an oblique angle.

Names of the planes:—

$$\begin{aligned} c &= c : \infty a : \infty b \\ d &= a : c : \infty b \\ g &= a : b : \infty c \\ 2g &= 2a : b : \infty c \end{aligned}$$

The oblique rhombic prism $2g$ is terminated by the end planes c in such a manner, that the crystals present a tabular appearance. The acute edges of the prism are truncated by

the planes d and g . The planes g do not present themselves at all, or if so, it is in the form of small triangles.

From the measurement of the angles result the following relation between the axes:— $b : a : c = 1 : 0.989 : 0.843$, and the angle between the axes c and $b = 72^\circ 20'$.

This salt is isomorphous with the hydrochlorate of chloraniline. It belongs to the same crystalline system, and is formed by the same planes. Still the character is somewhat different, viz. the crystals are less extended in the direction of the axis b , so that the horizontal edge, in which the two planes a cut each other, disappear, and the two planes d with the two g form a four-sided summit: the angle of the prism $2g : 2g$ was found here = $127^\circ 48'$. The angles of this salt however can not be so well measured as in the analogous one.

The analysis of the hydrochlorate of bromaniline gave the following results:—

1.1425 gram. of the salt gave 0.798 gram. of chloride of silver.

This corresponds to the formula $\text{Cl H, C}_{12} \left\{ \begin{smallmatrix} \text{H}_6 \\ \text{Br} \end{smallmatrix} \right\} \text{N}$, as is shown by the following calculation:—

		Theory.	Experiment.
1 equiv. Base	$= 2130.35$	82.40	
1 ... Hydrochloric acid	$= 455.15$	17.60	17.71
1 ... Hydrochlorate of Bromaniline }	$= 2585.50$	100.	

Bromaniline and Bichloride of Platinum,

is precipitated by mixing hydrochlorate of bromaniline with bichloride of platinum, and cannot be distinguished either in its relations or aspect from the platinum salt of the corresponding chlorine base. The analysis already given by the determination of the atomic weight furnished 26.19 per

294 Dr. Hofmann on the *Metamorphoses of Indigo*.

cent. platinum, from which is deduced the formula $\text{Cl H, C}_{12} \left\{ \begin{smallmatrix} \text{H}_6 \\ \text{Br} \end{smallmatrix} \right\} \text{N} + \text{Cl}_2 \text{Pt}$, which requires 26·22 per cent.

ACTION OF FUSED HYDRATE OF POTASH ON DIBROMISATINE
(*Bibromisatine*, Erdmann, *Bromisatinese*, Laurent).

F. *Dibromaniline* (*Amabrophenese*). $\text{C}_{12} \left\{ \begin{smallmatrix} \text{H}_5 \\ \text{Br}_2 \end{smallmatrix} \right\} \text{N}^*$

By the distillation of dibromisatine with hydrate of potash there passes into the receiver likewise an oily body, which solidifies into a crystalline mass. By washing these crystals with water till all trace of ammonia, which is formed in the last stage of the distillation, is removed, and dissolving in boiling alcohol, they are obtained of a shining white appearance.

a. Composition of Dibromaniline.

A very sure conclusion on the composition of this body may be drawn from analogy. I therefore contented myself with a determination of the carbon and hydrogen.

On burning with chromate of lead the following results were obtained :—

0·2795 grm. of the substance gave 0·2950 grm. of carbonic acid and 0·065 grm. of water. These numbers correspond in the 100 parts to

Carbon	28·77
Hydrogen	2·40

Corresponding formula, $\text{C}_{12} \left\{ \begin{smallmatrix} \text{H}_5 \\ \text{Br}_2 \end{smallmatrix} \right\} \text{N}$, as is shown by the following :—

		Theory.	Experiment.
12 equiv. Carbon . .	=	900·00	28·77
5 ... Hydrogen . .	=	62·50	2·40
2 ... Bromine . .	=	1956·62	
1 ... Nitrogen . .	=	177·05	
1 ... Dibromaniline	=	3096·17.	

* The dibromisatine employed was prepared by long digestion of bromisatine with bromine. The substance crystallized from alcohol and burned with chromate of lead gave the following results :—

0·406 grm. of substance gave 0·4715 grm. of carbonic acid and 0·047 grm. of water. These numbers correspond in the 100 parts to

Carbon	31·62
Hydrogen	1·28

and indicate the formula $\text{C}_{16} \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Br}_2 \end{smallmatrix} \right\} \text{NO}_4$, which requires

Carbon	31·83
Hydrogen	1·00

b. Properties of Dibromaniline.

These I have not as yet very carefully studied. They resemble in many respects those of bromaniline. The crystals of this body, however, have a totally different form. It does not crystallize in octahedrons as the bromaniline, but in flat, four-sided, rhombic prisms of considerable size, which unfortunately present no terminal planes.

The base is soluble in spirits of wine and yields successive crops of crystals to the last drop. It is only slightly soluble in boiling water, which becomes turbid on cooling, and deposits gradually fine white needles. The crystals of the base melt, between 50° and 60° cent., to a dark oily fluid, which frequently on cooling remain long liquid, but on agitation suddenly solidify to a crystalline mass.

A solution of the base in acids communicates, like aniline, a yellow colour to fir-wood and the pith of the elder tree.

The compounds of dibromaniline have likewise as yet not been the object of particular study. I will only mention a few observations which appeared to me essential to the establishment of the chemical characters of dibromaniline.

It possesses the properties of a base; its basic character is however much less pronounced than that of bromaniline. It dissolves in acids, and is again precipitated by alkalis. Its solution in hydrochloric acid gives with perchloride of iron the crystalline orange-yellow precipitate, characteristic of organic bases. It forms with acids crystalline salts, but these compounds possess much less stability than the corresponding salts of bromaniline.

A solution of the base in boiling hydrochloric acid deposits on cooling a salt which crystallizes in plates.

0.2313 grm. of these crystals, precipitated with nitrate of silver, gave 0.1205 grm. of chloride of silver, corresponding to 13.21 per cent. of hydrochloric acid. This determination leads to the formula $\text{Cl H, C}_{12} \left\{ \begin{smallmatrix} \text{H}^5 \\ \text{Br}_2 \end{smallmatrix} \right\} \text{N}$, as is seen by the following:—

	Theory.		Experiment.
1 equiv. Base . . .	= 3096.17	87.19	
1 ... Cl H . . .	= 435.15	12.81	13.21
1 ... Hydrochlorate of dibromaniline }	= 3551.32	100.00	

This substance is decomposed by the action of warm water. The base separates from the acid and swims on the surface of the fluid in the form of oily drops. This want of stability in the hydrochloric compound is also seen when the base is dis-

296 Dr. Hofmann on the Metamorphoses of Indigo.

solved in a great excess of acid and placed under a bell-glass with caustic lime. After some time crystals are obtained, which are only slightly soluble in water, and consist almost entirely of pure base. The elasticity of the hydrochloric acid is thus sufficient to overcome the affinity between it and the base.

G. Tribromaniline (*Amabrophenose*). $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Br_3 \end{smallmatrix} \right\} N$.

This compound has been long since described by Fritzsche* and named by him bromaniloid. He obtained it by treating aniline with bromine. It forms with the same facility by the action of the same body on bromaniline or dibromaniline.

I have prepared this body from bromaniline. The hydrochlorate of this base gives with a solution of bromine in water a white precipitate with a tint of violet. As the violet colour did not disappear by re-crystallization from alcohol, I submitted the compound to distillation. At the commencement of the distillation there are condensed in the receiver beautiful snow-white crystals; towards the end however the violet accessory product also passed over, and could not be removed again by recrystallization from alcohol. Although the properties and mode of formation of this body left no doubt of its identity with bromaniloid, I however made a combustion of it. Unfortunately, as stated, the substance was not perfectly pure, hence the proportion of carbon is too high.

0.3305 grm. of substance gave 0.2800 grm. of carbonic acid and 0.0450 grm. of water; corresponding in the 100 parts to

Carbon 23.10

Hydrogen 1.51

The formula will therefore be $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Br_3 \end{smallmatrix} \right\} N$, which requires

Carbon 22.15

Hydrogen 1.22

Tribromaniline is not a base but an indifferent substance, and does not combine with bases or acids. I must refer to Fritzsche's memoir for the description of its properties.

The following table exhibits the formulæ of the different bodies which form the subject of this paper:—

Substitution of the hydrogen by chlorine.

* *Bullet. Scient. de St. Pétersb.*, 1843, t. i. p. 30.

Substitution of the hydrogen by chlorine and bromine.

Substitution of the hydrogen by bromine.

We now return to the question, can chlorine play the part of hydrogen in organic compounds?

The isatine group is perhaps quite capable of affording some explanation of this question.

In isatine we have a body which, by the action of chlorine, loses one or more equivalents of hydrogen, which are replaced by the acting substance. These three compounds, isatine, chlorisatine and dichlorisatine, possess the same chemical and physical properties. By the substitution of chlorine for hydrogen the character of isatine has not been changed. Isatine, chlorisatine and dichlorisatine, by the action of other agents, suffered similar changes. By treatment with sulphuret of ammonium we see these three bodies assuming one equivalent of hydrogen and changing into isatyd, chlorisatyd and dichlorisatyd. By proper treatment with sulphuretted hydrogen the whole or part of the oxygen can be eliminated and replaced by sulphur. In contact with alkaline sulphates the sulpho-isatinic and chlorisatinic salts are formed; peculiar compounds, in which the sulphurous acid is united in a singular manner with the organic substance. The behaviour of isatine and chlorisatine to ammonia and alkalies is also similar: particularly towards the latter the analogy in their action is in the highest degree characteristic. At the ordinary temperature they unite directly with the alkalies, but at a boiling heat they change into isatinic and chlorisatinic acid, whose strict analogy in all these salts never fails. Finally, by fusion with hydrate of potash, we see isatine converted into aniline; when chlorisatine is treated in the same manner, still under conditions which certainly are favourable to fix the chlorine, this

element is observed to pass over into the new compound. From the fused hydrate of potash, which retains a portion of the carbon of chlorisatine in the form of carbonic acid, there distils over chloraniline, and with it the whole of the chlorine existing in the former compound. In the present memoir I have had frequent occasion to show the analogy which exists between aniline and the chlorinated base; it extends not only to the fundamental properties of both bodies, but even to the products of decomposition. By the action of bromine on aniline tribromaniline is formed, $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Br_3 \end{smallmatrix} \right\} N$; with the chlorinated base the same body gives chlorodibromaniline, $C_{12} \left\{ \begin{smallmatrix} H_4 \\ Cl \\ Br \end{smallmatrix} \right\} N$, which in no respect, either in its properties or characters, can be distinguished from the preceding. The only difference of the two compounds consists in the presence of chlorine in the second body.

On the preceding facts, when considered together, it appears to me that no two constructions can be entertained. They prove, in an undoubted manner, that in certain circumstances chlorine or bromine can perform the part of hydrogen in organic compounds.

It is quite another question, Is every organic body capable of assuming chlorine in the place of its hydrogen?

Further, in those organic compounds in which we see one or two equivalents of hydrogen replaced by chlorine, without any essential modification of their fundamental characters, is it possible to make a complete substitution of these elements without changing the properties of the compounds?

For the definite solution of these questions many further investigations must still be made. From the foregoing experiments it appears, however, that the chlorine preserves, to a certain extent, its electro-negative character in those compounds in which it replaces hydrogen, and that in proportion to the increase in the number of equivalents of the latter for which chlorine or bromine are substituted, so is this character the more impressed on the resulting compounds. The compound atom aniline, $C_{12} H_7 N$, in consequence of the peculiar arrangement of its elements, possesses the property of uniting with an acid; replace one equivalent of its hydrogen by bromine, and we obtain bromaniline; a body possessing likewise basic properties, but in a feebler degree. A number of metallic oxides, which can be precipitated from their solutions by aniline, are not affected by the brominated base. Bromaniline is a less powerful base than aniline. By the assumption

of the equivalent of the electro-negative body bromine, the basic properties of the original system is enfeebled; substitute now another equivalent of bromine for hydrogen, and we have dibromaniline. The facility with which, as we mentioned, all its salts are decomposed, evidently indicates that the basic character of aniline is further enfeebled by the repeated assumption of bromine. Finally, in tribromaniline the electro-negative properties of the assumed bromine equivalents have placed themselves in equilibrium with the electro-positive character of the original system. Possibly, by the further addition of bromine, a body may be formed possessing acid properties.

We have in inorganic chemistry the compounds of many metals with oxygen which exhibit in a distant degree the same character; for distant I must call it, since it is not a question of substitution. Protoxide of manganese is a strong base, whilst in the sesquioxide, richer in oxygen, the basic properties are lessened; peroxide of manganese unites with neither base nor acid, and by the addition of more oxygen we have manganic and hypermanganic acid generated.

It is only with the greatest diffidence I venture to express an opinion on this subject: nothing is more dangerous than to wish to draw general conclusions without having a mass of facts at command.

Bromaniline and dibromaniline possess, though in a lesser degree, the fundamental properties of aniline—they are bases. Tribromaniline is neutral; in it the original character of aniline has entirely disappeared. This body was however produced in a totally different way from that of the two brominated bases. It may be objected, that in it the grouping of the atoms, as they prevailed in the original system of aniline, no longer remained. Possibly there may exist a body of the same composition having the formula $C_{12}\left\{\begin{smallmatrix} H_4 \\ Br_3 \end{smallmatrix}\right\}N$, which still possesses basic properties. Such a body would be formed by distilling tribromisatine, $C_{16}\left\{\begin{smallmatrix} H_2 \\ Br_3 \end{smallmatrix}\right\}NO_4$, with hydrate of potash. This compound is as yet unknown. Further experiments must therefore be made to solve the question.

Before concluding this memoir I shall mention another compound which appears worthy of the attention of chemists.

It is formed by passing into aniline free from water a stream of cyanic acid obtained by distilling cyanuric acid. The fluid becomes considerably heated, and solidifies on cooling into a crystalline mass. These crystals are insoluble in water, but soluble in boiling alcohol, from which they are deposited in

white shining plates. It contains neither cyanic acid nor aniline. It may be heated with hydrochloric acid or potash without decomposition. It is a kind of urea, in which the ammonia is replaced by aniline. I was in hopes that this body would possess basic properties, and like urea form crystalline salts with nitric and oxalic acid; its properties are however totally different.

I shall in a separate memoir return more fully to this product of the decomposition of aniline.