

current, the other might be unable to resist attack. There was no comparison between the position of the stomach and that of the rabbit's ear, and the question, according to his view, resolved itself into degree of power possessed by the acidity of the contents of the stomach on the one hand, and the alkalinity of the circulating current on the other.

The author concluded by adducing experimental evidence to show that pepsine was contained in the walls of the stomachs of persons who had died from severe diseases, as well as in the normal fasting and digesting stomach.

January 15, 1863.

Major-General SABINE, President, in the Chair.

The following communications were read :—

- I. "Notes of Researches on the Poly-Ammonias.—No. XXII. Secondary Products formed in the Manufacture of Aniline." By A. W. HOFMANN, LL.D., F.R.S. Received December 18, 1862.

In a short paper submitted to the Royal Society some weeks ago, I have recorded some experiments on the basic compounds distilling at very high temperatures, which are formed as secondary products in the manufacture of aniline, and which are known in the ateliers of MM. Collin and Coblenz as *queues d'aniline*. I have mentioned that the bases which distil above  $330^{\circ}$ , when treated with dilute sulphuric acid, furnish a soluble sulphate, the sulphate of paraniline, the history of which I have already traced, and a sulphate remarkable for its insolubility in water. It is this insoluble sulphate, and the base from which it is derived, that form the subject of the following notice.

The insoluble sulphate which is formed on treating the *queues d'aniline* boiling above  $330^{\circ}$  with cold dilute sulphuric acid, separates as a yellowish semisolid crystalline mass, contaminated with considerable quantities of the oily sulphates of other bases. Ebullition with alcohol removes these substances pretty well, and the sulphate becomes more crystalline and nearly white. A further purifi-

VOL. XII.

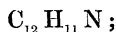
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cation is effected by dissolving this mass in a large quantity of boiling water, and filtering from insoluble oily substances; on cooling, the sulphate separates in white needles, which, on boiling with alcohol, become perfectly pure.

In order to liberate the base, the sulphate is suspended in weak alcohol, and submitted to the action of caustic soda: a solution is thus obtained, which, on the addition of water, deposits the new base in scaly crystals. They require only to be washed with water, to be redissolved in alcohol, and to be reprecipitated by addition of water.

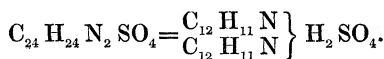
Thus obtained, this substance presents itself in small white needles or scales, which are apt to assume a greyish tint on drying, very slightly soluble in boiling water, easily in alcohol and ether. This base fuses at  $45^{\circ}$ , and boils at  $322^{\circ}$ , distilling without the slightest alteration.

The numbers obtained in the analysis of this substance may be translated into the formula



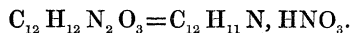
and this expression is unmistakeably corroborated by the examination of several well-defined saline compounds, more especially the sulphate, chloride, and nitrate.

*Sulphate*.—This salt, repeatedly mentioned, is remarkable for its very sparing solubility in cold, and even boiling water; the boiling aqueous solution deposits small needles of the composition

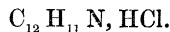


This salt is somewhat more soluble in alcohol.

*Nitrate*.—Large white plates, moderately soluble in water, which are obtained by dissolving the base in dilute nitric acid, and recrystallizing the first crop of crystals from boiling water. Composition:

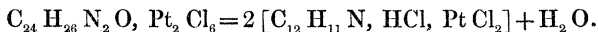


The *chloride* is readily obtained in small white needles, somewhat more soluble in water than the sulphate. It was found to contain at  $100^{\circ}$ ,

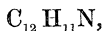


The *platinum-salt* falls as a precipitate of a pale yellowish colour with a tint of grey, which under the microscope is found to consist

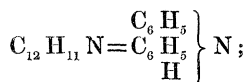
of small crystalline needles. This salt contains water of crystallization, which it does not lose even at  $150^{\circ}$ . Dried respectively at  $110^{\circ}$ ,  $120^{\circ}$ ,  $130^{\circ}$ , and  $150^{\circ}$ , it invariably exhibited the composition



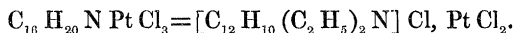
The interpretation of the formula



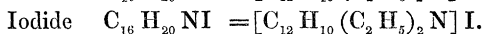
established by these well-concordant analyses, appeared to present no difficulties. The origin of the compound, although uncertain, is surrounded by phenylic associations; and nothing, in fact, could have been more natural than to consider the new base as *diphenylamine*,



this view, moreover, appeared to be countenanced by the deportment of the compound under the influence of iodide of ethyl. To secure at once the last term of ethylation, the base was repeatedly submitted in alcoholic solution to the alternate action of iodide of ethyl and oxide of silver. The product of the reaction was by appropriate treatment converted into a platinum-salt, which was found to be but slightly crystalline, insoluble in water, but readily soluble in alcohol. Both combustion and platinum-determination proved this salt to contain



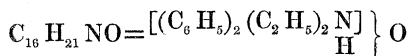
This salt was decomposed by sulphuretted hydrogen, and successively treated with oxide of silver and iodide of ethyl, chloride of silver and dichloride of platinum, so as to produce in succession the chloride and oxide and, lastly, the iodide, chloride, and platinum-salt of a higher ethylated body. But the platinum-salt thus obtained was found to have still the same composition, which was, moreover, confirmed by the analysis of a fine *bromide*, crystallizing in prisms, difficultly soluble in water and ether, but easily soluble in alcohol, and a well-defined *iodide*, crystallizing in plates and having properties similar to those of the bromide. These salts contained respectively,



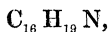
But before admitting these substances to be truly diethyl-diphenyl-

lated ammonium compounds, it appeared desirable to prepare the oxide corresponding to these salts. On treating the alcoholic solution of the bromide or iodide with oxide of silver, a liquid was formed which showed *no* alkaline reaction, and which, on evaporation, deposited white needles, insoluble in water, moderately soluble in alcohol, easily soluble in ether, which fused at  $100^{\circ}$  and volatilized at a higher temperature without decomposition.

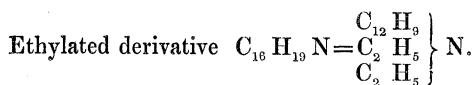
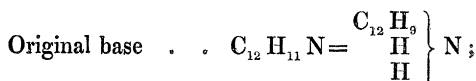
These are not the properties of a tetrasubstituted ammonium base; moreover the combustion led, instead of to the formula



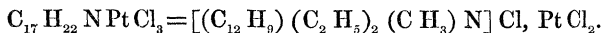
flowing out of the above conception, to the expression



incompatible with this conception, and revealing at once the true nature both of the original base and its ethylated derivative. The former is a primary, the latter a tertiary monamine:



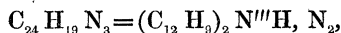
To remove a last doubt which might have been entertained, it became desirable to prove that this latter base could fix another molecule of the iodide of an alcohol radical. Having failed with iodide of ethyl, I tried the action of iodide of methyl, which stands so much closer to hydriodic acid, and was delighted to find that the base is attacked by this compound, the product being an iodide which, when treated with oxide of silver, yielded a powerfully alkaline solution, possessing all the characters of the free ammonium bases. Converted into a chloride and precipitated by dichloride of platinum, this substance furnished a difficultly soluble platinum-salt crystallizing in needles, the combustion and platinum-determination of which gave numbers unequivocally fixing the formula



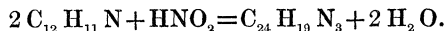
These results show how much preferable, on the whole, for fixing the degree of substitution in ammonias is iodide of methyl, although

the numbers which the methylated compounds furnish are of necessity less characteristic than those of the ethylated derivatives.

The new base, for which I propose the name Martylamine, is remarkable for the disinclination with which it goes through the series of performances which are generally expected from well-defined monamines. Chlorine, bromine, and oxidizing agents in general, give rise to the formation of dark-coloured compounds, which appear to possess but little tendency to crystallize. An exception is formed by its behaviour with nitrous acid. On passing this gas through an alcoholic solution, the liquid becomes warm, and soon solidifies into a mass of red crystals, which are insoluble in water, difficultly soluble in alcohol, easily soluble in ether, which contain



showing that this substance is formed by simple nitrogen substitution, which in this case links two molecules of martylamine together,



Treated with acids, this substance is easily reconverted into martylamine with simultaneous formation of an aromatic compound, which I intend to examine more minutely by-and-by.

I cannot at present offer any observation on the reaction which in the manufacture of aniline gives rise to the formation of the new base, although MM. Collin and Coblenz have most kindly furnished me with a detailed account of the several phases of their operations. It might, in fact, at the first glance appear to be waste of time to examine a compound which, however well defined, may owe its formation to a combination of conditions which are not easily realized again. My friends Mr. Nicholson and Mr. Perkin, of well-known experience in matters connected with the manufacture of aniline, have never observed this compound in their operations. Martylamine, nevertheless, is endowed with an interest of its own. Though of obscure origin, this body, from the place it occupies on the ladder of carbon, and from its very composition, establishes at once ties of parentage with some of the most distinguished families in the domain of organic chemistry. A glance at the formula of martylamine suffices to point out the close connexion of this compound with *benzidine*, the remarkable base obtained by Zinin from azobenzol, and the true constitution of which was lately made out in

my laboratory by Dr. P. W. Hofmann. These two compounds stand in the same relation to each other as ethylamine and ethylene-diamine, as phenylamine and phenylene-diamine :



This is not merely a relationship existing on paper; whoever has had these compounds in his hand will at once recognize the necessity of placing them side by side; but I may be allowed to point more particularly to the remarkable similarity of the deportment of benzidine under the influence of iodide of ethyl, this base exhibiting the same reluctance to pass from the state of tertiary substitution to the state of ammonium base—a passage which, in the case of benzidine, exactly as in the case of martylamine, had to be accomplished by means of iodide of methyl.

II. "On the Form of Crystals of Peroxide of Benzoyl." By  
WILLIAM HALLOWS MILLER, M.A., For. Sec. R.S., Pro-  
fessor of Mineralogy in the University of Cambridge.  
Received December 18, 1862.

The peroxide of benzoyl,  $\text{C}_{14} \text{H}_{10} \text{O}_4$ , or carbon 69·42, hydrogen 4·13, oxygen 26·45, was discovered by Professor (now Sir B. C.) Brodie, and described by him in the 'Proceedings' of the Royal Society, vol. ix. p. 361. The crystals were obtained from a solution in ether of the product of the mutual decomposition of equivalent proportions of chloride of benzoyl and peroxide of barium mixed in water. The faces of the crystals, though brilliant, were not very even, so that, in order to obtain a moderately accurate result, it was necessary to measure a large number of crystals. The column headed 'observation' contains the means of the observed angles; the column headed 'calculation,' the most probable values of the angles, taking into account the quality of the faces containing them, and the number of the observations in each case.

System prismatic:—

$$101, 001 = 33^\circ 24'; \quad 110, 100 = 57^\circ 50'5.$$