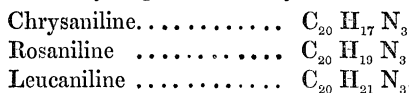


monochloroplatinate and a dichloroplatinate, combining with more or less water of crystallization.

The composition of chrysaniline places this substance in immediate juxtaposition with rosaniline and leucaniline. These three triamines simply differ by the amount of hydrogen which they contain.



Chrysaniline is monacid or diacid; rosaniline monacid or triacid, but with essentially monacid predilections; leucaniline forms exclusively triatomic compounds.

The formula of chrysaniline suggests the possibility of transforming this substance into rosaniline and leucaniline, or of producing chrysaniline from rosaniline or leucaniline. Up to the present moment this transformation has not been experimentally accomplished. The constitution and genesis of chrysaniline remain to be made out.

VI. "Researches on the Colouring Matters derived from Coal-tar.—
II. On *Aniline-blue*." By A. W. HOFMANN, LL.D., F.R.S.
Received June 30, 1863.

Among the several stages which mark the development of the industry of coal-tar colours, the discovery of the transformation of aniline-red into aniline-blue will always hold a prominent position. This transition, for the first time observed by MM. Girard and De Laire*, two young French chemists of M. Pelouze's Laboratory, and subsequently matured by M. Persoz, De Laynes, and Salvétat†, has become the foundation of an enormous industrial production, which, having received a powerful impulse by MM. Renard Brothers and Franc in France, and more recently by Messrs. Simpson, Maule, and Nicholson in this country, has rapidly attained to proportions of colossal magnitude.

The transformation of aniline-red into aniline-blue is accomplished by a process of great simplicity, and consists, briefly expressed, in the treatment at a high temperature of rosaniline with an excess of aniline. The mode of this treatment is by no means indifferent. Rosaniline itself cannot in this manner conveniently be converted into the blue colouring matter; the transformation is, however, easily accomplished by heating rosaniline salts with aniline, or, *vice versâ*, rosaniline with salts of aniline. Again, the nature of the acids with which the bases are combined is by no means without influence upon the result of the operation; manufacturers give a decided preference to organic acids, such as acetic or benzoic acids.

The production of the new colouring matter on a very large scale has already elicited a good deal of most valuable information regarding the

* French patent, January 1861.

† Comptes Rendus, March and April 8th, 1861.

phenomena which characterize the transition of rosaniline into its blue derivative; again, the several processes of purification to which the crude product is submitted have thrown much light upon the chemical character of the compound.

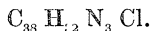
MM. Girard and De Laire, whose names are so intimately associated with the development of the new colour-industry, have pointed out that the passage from red to blue is attended by an evolution of torrents of ammonia; and Mr. Nicholson, who combines the genius of the manufacturer with the habits of the scientific inquirer, has ascertained that the blue colouring matter is invariably a *saline* compound of a base itself colourless, like rosaniline. But the relations between the two colourless bases, and consequently the nature of the reaction by which rosaniline is converted into the blue colouring matter, had hitherto remained unknown.

It was therefore with great pleasure that I accepted the kind offer of my friend Mr. Nicholson to supply me with the necessary materials for the elucidation of this question.

The salt transmitted to me, and which Mr. Nicholson had prepared himself, was the chloride.

Hydrochlorate.—This compound is an indistinctly crystalline powder of a bluish-brown colour, which at 100° becomes pure brown. It is perfectly insoluble in water, cold or boiling—so much so, indeed, that it imparts no colour to the water with which it is washed. It is likewise insoluble in ether, but dissolves, although with difficulty, in alcohol, which assumes the magnificent deep-blue tint characteristic of this colouring matter. The boiling saturated alcoholic solution deposits the chloride on cooling in the form of imperfect crystalline granules. The alcoholic solution, when evaporated, leaves the compound as a thin film, which reflects the light with a peculiar metallic, half-golden, half-coppery lustre.

The hydrochlorate has the same composition whether dried *in vacuo* or at 100°. Several analyses made with specimens of different preparations lead unmistakably to the expression

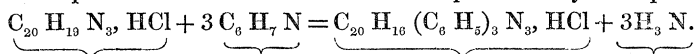


This formula contains the history of aniline-blue, pointing out as it does not only its chemical character and the relation in which it stands to rosaniline, but explaining also, in the most satisfactory manner, the reaction by which the passage from red to blue is accomplished.

The simple and natural interpretation of the formula which I have given, exhibits the new compound in the light of the hydrochlorate of triphenylic rosaniline*,



when the process of transformation becomes represented by the equation

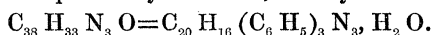


* The relation between aniline-red and aniline-blue is already pointed out in a short note submitted to the Royal Society a few weeks ago.—A. W. H.

Free Base.—The separation of the base from the hydrochlorate presents no difficulty. This salt dissolves in alcoholic ammonia, giving rise to a wine-yellow solution. This liquid contains the base in the free state, together with chloride of ammonium. On ebullition the blue colour reappears, the salt being reproduced with evolution of ammonia. Addition of water, on the other hand, produces a white or greyish precipitate, consisting of *triphenylic rosaniline*. The best mode of procuring this compound in a state fit for analysis is to pour the concentrated solution of the hydrochlorate in ammoniacal alcohol into water, when the base separates as a curdy mass which soon collects upon the surface of the liquid. During the process of washing, and especially of drying, even *in vacuo*, the greyish powder gradually assumes a blue tint. The vacuum-dry substance, when exposed to 100°, assumes a deep brown colour, which it retains on cooling; at 100° it slightly fuses, but does not change weight.

Triphenylic rosaniline shows a tendency to crystallize, but hitherto I have not been able to obtain it in distinct crystals. The solution in alcohol and also in ether (which dissolves the base with the greatest facility) have, even on spontaneous evaporation, deposited the base in the form of an almost amorphous residue.

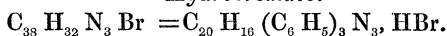
Analysis assigns to this base the composition which corresponds to that of the hydrochlorate previously examined, namely



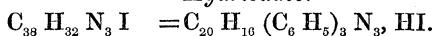
Triphenylic rosaniline is thus seen to separate from its saline combinations in the state of hydrate, exactly like rosaniline itself.

I have endeavoured to obtain further confirmation of these results by the analysis of several salts of triphenylic rosaniline. These salts were invariably prepared by treatment of the free base with the free acids. They resemble in their properties the hydrochlorate—so much so, indeed, that they could not possibly be distinguished without analysis. The nitrate is perhaps a little more, the sulphate a little less soluble in alcohol than the hydrochlorate. The following salts were submitted to analysis:—

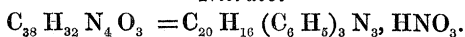
Hydrobromate.



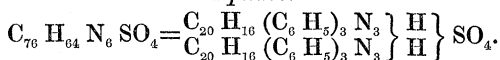
Hydriodate.



Nitrate.



Sulphate.



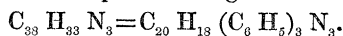
Rosaniline, it will be remembered, forms, in addition to its ordinary monatomic compounds, a series of triatomic salts, which are more soluble and comparatively colourless. I have vainly endeavoured to prepare similar compounds with the triphenylic derivative of rosaniline.

Action of reducing agents upon Triphenylic Rosaniline.—Remembering the facility with which rosaniline is attacked by reducing agents, and the valuable help which the examination of the leucaniline thus produced afforded in establishing the formula of rosaniline, I was led to study the deportment of the triphenylic derivative under similar circumstances. This substance indeed is readily reduced both by nascent hydrogen and by sulphide of ammonium.

The alcoholic solution of the chloride, when left in contact with zinc and hydrochloric acid, is rapidly decolorized. The clear liquid when mixed with water yields a white, scarcely crystalline precipitate, which may be freed from chloride of zinc by washing, and separated from accidental impurities by solution in ether, in which it is easily soluble.

If the reduction be effected by sulphide of ammonium, the product is apt to be contaminated with sulphur and secondary products. In this case the separation has to be accomplished by treating the crude mass obtained in the reaction with bisulphide of carbon, which dissolves both the sulphur and the product of the reduction, leaving behind a brown resinous substance, the nature of which is not yet investigated. The mixture remaining after the evaporation of the bisulphide of carbon is repeatedly boiled with soda, which dissolves the sulphur; the residuary compound is then finally purified by solution in ether, from which it is deposited on spontaneous evaporation in the form of a friable resin.

Unfortunately this compound is no longer basic, so that it was impossible to combine it with acids; but its combustion has furnished numbers agreeing exactly with the composition assigned to it by theory, namely



The compound accordingly is *triphenylic leucaniline*. It will be observed that the triphenylic derivative, like leucaniline itself, is anhydrous—a constancy of behaviour in the normal and derived compounds which has already been pointed out in the case of rosaniline and its phenylic derivative. Under the influence of oxidizing agents, the hydrogenetted body is rapidly reconverted into the compound from which it has been obtained. The experiment succeeds best with platinum-chloride. The colourless solution of triphenylic leucaniline, when boiled with a few drops of dichloride of platinum, immediately assumes the splendid blue colour which distinguishes the salts of the non-hydrogenetted base.

The transformation of aniline-red into aniline-blue possesses a variety of interests. A lively imagination might feel tempted to speculate on the relation between colour and composition; but there are other questions claiming more immediately the attention of the experimentalist.

Up to the present moment chemists were unacquainted with a method of *phenylation*. The chloride, bromide, and iodide of the phenyl-series have been but imperfectly studied; but we are sufficiently acquainted with them to know that they are far from possessing the plastic character of the corresponding compounds of the methyl- and ethyl-series, which

confers such value upon these substances as agents of research. We are unable to substitute phenyl for hydrogen by processes borrowed from the experience gathered in experimenting with the ordinary alcohols. Diphenylamine and triphenylamine are substances existing at present only in the conception of the chemist. It was reserved for the peculiar, I might almost say instinctive mode of experimenting belonging to industry to fill up this blank.

The transformation of rosaniline into aniline-blue suggests some other questions which must not altogether remain unnoticed here, although I hope to enter more fully into this subject elsewhere. Does this transformation simply involve an interchange between the hydrogen and phenyl atoms, or does the rosaniline molecule lose ammonia, which is replaced by aniline?

I do not pretend to answer this question; but I beg leave to record some experiments as materials towards the solution of the problem.

Methylic, Ethylic, and Amylic Derivatives of Rosaniline.

The interpretation of the results delineated in the previous pages legitimately suggested the study of the behaviour of rosaniline under ordinary processes of substitution—in other words, the treatment of this base with the iodides of methyl, ethyl, and amyl. I will not describe the pleasure with which I observed the intense blue colour of the mixture of rosaniline with these iodides when, after a day's digestion, I took the sealed glass tubes from the boiler. The action of iodide of methyl and ethyl is readily accomplished at 100° C.; iodide of amyl requires a temperature of from 150° to 160°. The presence of alcohol facilitates the reaction.

Up to the present moment I have only examined in detail the action of iodide of ethyl. The product of this action is an iodide which dissolves with a magnificent blue colour in alcohol. The tinctorial powers of this solution are scarcely inferior to that of rosaniline itself; and industry will probably not disdain to utilize this latest indication of science.

The blue ethylated derivative of rosaniline, as might have been expected, presents in its properties greater analogies with rosaniline itself than the triphenylic compound. This analogy suggested difficulties in the separation of the two substances which it appeared better to avoid. The iodide produced by the reaction was therefore at once decomposed by soda, and the ethylic derivative, together with the unaltered rosaniline, again submitted to the action of iodide of ethyl. After this process had been once more repeated, the alcoholic solution of the final product was precipitated by water, which separated a soft resin-like substance, solidifying on cooling with crystalline structure, and exhibiting a very peculiar metallic lustre intermediate between those presented by the salts of rosaniline and of its phenylic derivative. Crystallization from dilute spirit furnished the iodide in the pure state. The results obtained in the combustion and iodine determination of this substance agree with the formula



showing that the frequent repetition of the process of ethylation had produced, not the *hydriodate* of *triethylic rosaniline*, but the *ethyliodate* of this substance,—a result which appeared particularly welcome, inasmuch as it threw at the same time considerable light upon the degree of substitution which belongs to rosaniline itself.

The facts elicited by the study of the action of iodide of ethyl upon rosaniline open a new field of research, which promises a harvest of results. The question very naturally suggests itself, Whether the substitution for hydrogen in rosaniline of radicals other than methyl, ethyl, and amyl, may not possibly give rise to colours differing from blue; and whether chemistry may not ultimately teach us systematically to build up colouring molecules, the particular tint of which we may predict with the same certainty with which we at present anticipate the boiling-point and other physical properties of the compounds of our theoretical conceptions?

This idea appears to have floated in the mind of M. E. Kopp when, with remarkable sagacity, he concluded his paper on *Aniline-red** in the following terms:—"The hydrogen of this substance being replaceable also by methyl, ethyl, and amyl, &c., we may anticipate the existence of a numerous series of compounds, all belonging to the same type, and which might constitute colouring matters either red, or violet, or blue."

Conceptions which only two years ago appeared little more than a scientific dream, are now in the very act of accomplishment.

I propose to continue these researches, and intend in a later communication to submit to the Royal Society the results obtained in the study of two other colouring matters derived from rosaniline, viz. *aniline-green* and *aniline-violet*.

November 26, 1863.

Major-General SABINE, President, in the Chair.

In accordance with the Statutes, notice was given from the Chair of the ensuing Anniversary Meeting, and the list of Officers and Council proposed for election was read as follows:—

President.—Major-General Edward Sabine, R.A., D.C.L., LL.D.

Treasurer.—William Allen Miller, M.D., LL.D.

Secretaries.— $\left\{ \begin{array}{l} \text{William Sharpey, M.D., LL.D.} \\ \text{George Gabriel Stokes, Esq., M.A., D.C.L.} \end{array} \right.$

Foreign Secretary.—Prof. William Hallows Miller, M.A.

Other Members of the Council.—James Alderson, M.D.; George Busk, Esq., Sec. L.S.; Col. Sir George Everest, C.B.; Hugh Falconer, M.A., M.D.;

* Ann. de Chim. et de Phys. [3] lxii. 230.