

hydration is assimilated by the products of decomposition, the substitution of ethylic potassa for the hydrate appears in many cases to promise valuable results from this mode of ethylation. The facility, however, with which ethylic potassa decomposes at a comparatively low temperature, must always be a serious obstacle to an extensive use of this reaction.

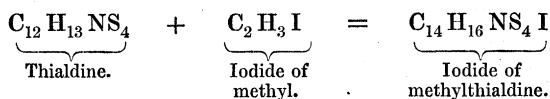
II. "Contribution towards the History of Thialdine." By  
A. W. HOFMANN, LL.D., F.R.S. Received May 30, 1857.

Researches into the behaviour of several organic bases with bi-sulphide of carbon, which I intend to lay before the Society at a later period, have led to some experiments with thialdine, the results of which I may be allowed briefly to state, since they are but loosely connected with the principal object of the inquiry.

It appeared of interest to gain some insight into the constitution of thialdine, which is the prototype of an important class of alkaloïds containing sulphur. To what group of bases does this body belong? Is it a primary, a secondary, or a tertiary base? The favourite method of questioning bases by means of iodide of methyl promised to furnish some elucidation of this subject.

Thialdine, dissolved in iodide of methyl, to which conveniently its own bulk of ether has been added, furnishes after twelve hours a solid crystalline mass, which may be readily freed from adhering thialdine by washing with ether and recrystallizing from alcohol.

The crystalline compound produced in this manner is the iodide of a methylated base, generated, as proved by analysis, by the union of equal equivalents of the two constituents.

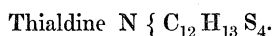
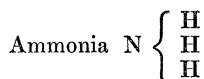


The deportment of the new iodide resembles that of iodide of tetramethylammonium, and the analogous iodides, which I have described some years ago. Insoluble in ether, soluble in alcohol, and precipitated from this solution by ether in the crystalline state, soluble in water with an acid reaction, and separated from it again,

unchanged by potassa in the cold, this substance exhibits in general all the characters which distinguish the iodides of the so-called ammonium-bases.

The great mobility of the elements in thialdine, and especially the large amount of sulphur which it contains, afforded but little hope of successfully submitting the new iodide to the experiment with oxide of silver, which is so characteristic for the ammonium-bases. On adding oxide of silver to the aqueous solution of this body, which, as has been remarked already, possesses an acid reaction, iodide of silver is formed, and the liquid assumes at once a marked alkaline reaction; but since the almost simultaneous formation of sulphide of silver, and a powerful evolution of aldehyde, sufficiently indicate the perfect destruction of the compound, and since experiment denotes the presence of ammonia in the liquid, it is impossible to decide whether the alkaline reaction observed after decomposition is due to the liberation of an ephemeral ammonium-base, or to its product of decomposition.

My experiments appear nevertheless to establish that thialdine belongs to the tertiary bases,—that it is a nitrile-base.

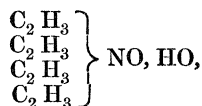


To the complex molecule,  $\text{C}_{12} \text{H}_{13} \text{S}_4$ , we must ascribe the faculty of replacing the 3 equivalents of hydrogen in the ammonia. In what manner, however, the elements are grouped in this complex molecule, whether we have here to assume a very unstable tribasic radical, or whether special molecules are inserted for each of the hydrogen-equivalents in the ammonia;—to decide these points further experiments are required.

Liebig and Wöhler, in their memoir on thialdine, state that the whole of the nitrogen of this base is eliminated in the form of ammonia, if the compound be decomposed by nitrate of silver. This deportment appeared to furnish an easy mode of controlling the formula of methylthialdine; after the decomposition of this body by nitrate of silver, I expected to find the whole of the nitrogen in the residuary liquid in the form of methylamine. On performing

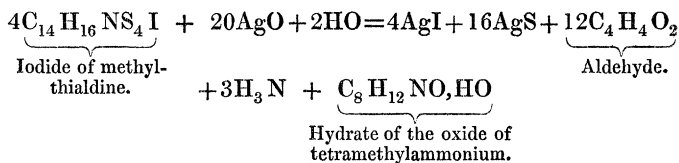
the experiment, it was found that the liquid contained considerable quantities of ammonia, but together with the latter alkali a fixed base. This unexpected deportment reminded me of experiments published several years ago\*, on the action of oxide of silver on thialdine, which is said to be thus converted into *Leucine*. The question presented itself, were the phenomena observed in the present case of an analogous character? had the above experiment given rise to the formation of methylated *Leucine*?

Experiment proved that the decomposition of iodide of methylthialdine by oxide of silver gives rise to the formation of ammonia and of the oxide of tetramethylammonium



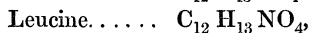
which was satisfactorily identified by the analysis of the gold- and platinum-compound.

The following equation represents this change :—



The absence of any leucine-like compound among the products of decomposition of iodide of methylthialdine induced me to repeat the experiment on the action of oxide of silver upon thialdine itself.

The transformation of thialdine into leucine, announced several years ago, and apparently very intelligible by the analogy of the formulæ of the two bodies



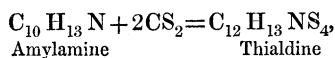
has not failed to rivet the attention of chemists. I wonder how such an error could have crept into science; for I have convinced myself, by a series of careful experiments, that this assertion is without the slightest foundation.

Thialdine, when treated with oxide of silver, as might have been

\* Goessmann, Liebig's Annalen, xc. 184.

expected, undergoes the same decomposition which Liebig and Wöhler had effected by means of nitrate of silver. It furnishes in this process aldehyde, acetic acid, and ammonia, but *no leucine*.

In conclusion, a remark which refers to a question connected with this alleged formation of leucine:—Soon after the statement regarding this subject had been made, Wagner\* observed that the action of bisulphide of carbon upon amylamine gives rise to the formation of a crystalline compound. This compound was not analysed, but Wagner suggested that possibly it might be thialdine,



and that in case this assumption proved to be correct, the action of bisulphide of carbon upon the homologues of ammonia might lead to the artificial formation, not only of leucine, but of glycocine, alanine, &c.

During my experiments on the deportment of bisulphide of carbon with organic bases, I have also had occasion to study the compound of amylamine with bisulphide of carbon. It is only necessary superficially to compare this substance with thialdine, in order to perceive at once that they are two absolutely different compounds; and if there is still a chance of producing leucine from amylamine, it is because the action of bisulphide of carbon does *not* give rise to the formation of thialdine.

### III. "On the Action of Sulphuric Acid upon Anisic and Salicylic Acids." By A. W. Hofmann, LL.D., F.R.S. Received June 5, 1857.

In a paper read before the Royal Society, we have, Mr. Buckton and myself, directed attention to the general occurrence of the disulpho-acids, of which only few and scattered examples were known at that time.

M. Louis Zervas has since continued the study of this subject in my laboratory, and has arrived at the following results.

\* Journal für praktische Chemie, lxi. 505.