

December 5, 1872.

Rear-Admiral G. H. RICHARDS, C.B., Vice-President, in
the Chair.

It was announced from the Chair that the President had appointed as
Vice-Presidents :—

The Treasurer.
Mr. Busk.
Dr. Hirst.
Admiral Richards.
Dr. Sibson.

The following communications were read :—

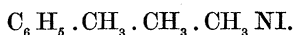
- I. "Synthesis of Aromatic Monamines by Intramolecular Atomic
Interchange." By A. W. HOFMANN, M.D., LL.D., F.R.S.
Received August 22, 1872.

In a paper submitted to the German Chemical Society about a year ago, we proved (Dr. Martius and myself*) that the action of methylic alcohol on aniline chlorhydrate at a high temperature and under pressure, far from yielding exclusively methyl- and dimethylaniline, as had been formerly believed, is capable of causing methylation of the phenyl group, and thus producing quite a series of higher homologues of dimethylaniline.

If we endeavour to gain an insight into the mechanism of this reaction, we are led to assume that in the first instance the chlorhydric acid of the aniline salt gives rise to the formation of methylic chloride, which in its turn induces substitution, first in the ammonia fragment, and ultimately in the phenyl group itself. If, on the other hand, we remember that a tertiary monamine, such as must be formed by the final methylation of the ammonia fragment in aniline, when submitted to the action of an alcohol chloride, is invariably converted into an ammonium compound, it must appear rather strange that, in the process above alluded to, only tertiary, and never any quartary bases are observed.

Under these circumstances the idea very naturally suggested itself of submitting the behaviour of quartary compounds at a high temperature under pressure to an experimental investigation.

The simplest compound that could be selected for such an inquiry appeared to be trimethylphenylammonium iodide.



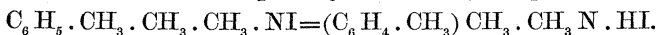
Reserving for a future communication the experimental details of this

* Hofmann and Martius, *Berichte*, 1871, p. 742.

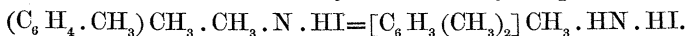
inquiry, I will limit myself for the present to a brief statement of the principal results obtained.

Leaving secondary reactions out of consideration, the transformation of the trimethylated phenylammonium iodide is represented by the following equations :—

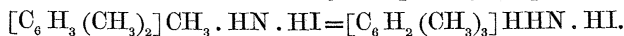
Transformation of quartary into tertiary compound.



Transformation of tertiary into secondary compound.



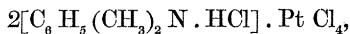
Transformation of secondary into primary compound.



Accordingly trimethylated phenylammonium iodide, when submitted to the action of heat, is transformed, in the first place, into iodhydrate of dimethylated methylophenylamine or dimethyltoluidine; this, in a second phase of the reaction, becomes iodhydrate of monomethylated dimethylophenylamine or methyl xylidine, which in its turn is ultimately converted into iodhydrate of trimethylophenylamine, *i. e.* of cumidine. The essential character of the reaction is thus seen to be an intramolecular change in the position of the methyl groups. According to the duration of the process, there are incorporated in the benzol nucleus, first the methyl group of the alcohol iodide, and then successively the two methylic groups which are stationed in the ammonia fragment. The action of heat on the quartary ammonium compound thus places at our disposal a simple means of rising from the benzol series itself to the toluol, xylol, and cumol series, or, generally (for the reaction may probably be utilized in many other cases), of passing from a less carbonated to a more carbonated series of compounds.

In carrying out the researches, the general results of which are sketched in the preceding paragraphs, rather considerable quantities of trimethylated phenylammonium iodide were consumed. This I obtained partly by methylating pure aniline with methyl iodide, partly by starting from commercial dimethylaniline, which was most liberally supplied to me by my friends Drs. Martius and Mendelssohn Bartholdy, having been specially purified for this purpose by Mr. G. Krell, by fractional distillation in the laboratory of the factory. This purified material was found to boil between 192° and 200°; and only few rectifications were necessary in order to obtain from it dimethylaniline in a state of perfect purity, identical in every respect with the base prepared by submitting trimethylated phenylammonium hydrate to distillation. Pure dimethylaniline is a liquid of 0.9553 volume weight, solidifying to a crystalline mass at +0°.5, and boiling

at 192°. The boiling-point was repeatedly determined, since it had been erroneously stated by M. Lauth* to be 202°. The nature of the compound was ascertained by the analysis of the beautiful platinum salt



crystallizing in well-formed tables of considerable solubility.

In the early experiments trimethylated phenylammonium iodide was employed in the pure state, such as is obtained by crystallization; subsequently, however, it was found to be quite sufficient if 1 mol. of dimethylaniline was mixed with 1 mol. of methyl iodide, and the compound thus produced at once submitted to the action of heat.

The quartary iodide may be exposed to a temperature of 200° for a considerable time without undergoing any alteration; but when heated for a day to from 220° to 230°, the salt is changed, the whole crystalline compound being transformed into an amber-yellow viscid mass, exhibiting no longer a trace of crystalline structure. If the temperature be then raised to the melting-point of lead (335°), a further change is manifested by the amorphous resinous substance having solidified again to a hard mass of large radiated, generally rather coloured crystals. On opening the digestion-tubes, appreciable quantities of unflammable gas are evolved.

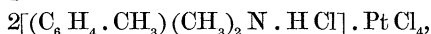
The products formed at moderate and extreme temperatures essentially differ from one another. This is seen at once when the iodhydrates produced in both cases are decomposed by alkali, and the bases thus liberated are submitted to distillation in a current of steam. The volatility of these bases shows the absence of quartary compounds; but whilst the monamines formed at moderate temperatures unite with acids to extremely soluble salts, which are scarcely to be crystallized, those which are produced at high temperatures are found to solidify to rather difficultly soluble, readily crystallizable salts with acids. The former bases exhibit the characters of *tertiary* and *secondary*, the latter ones those of *primary* monamines. Under these circumstances, it appeared desirable separately to examine the products formed in different conditions of temperature.

Examination of the Monamines formed at moderately High Temperatures.

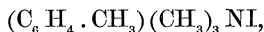
On submitting the iodhydrates formed at 220°–230° to distillation with alkali, a basic oil is obtained which, when rectified after drying over hydrate of potassium, boils between 200° and 280°. By repeated distillation the boiling-point is considerably lowered, small quantities of substances boiling beyond the range of the thermometer being separated. Finally, by far the greater portion of the bases is found to pass between 186° and 220°. This liquid consists of two varieties of dimethyltolui-

* Lauth, Bull. Soc. Chim. [2] vol. vii. p. 448.

dine, of methylxylidine, and small quantities of dimethylxylidine. Of the two dimethyltoluidines, the one has the vol. w. 0.9324, and boils constantly at 186°; the other has the vol. w. 0.9368, and boils at 205°, *i. e.* 19° higher than the former one. The nature of these two bases was fixed by the analysis of their platinum salts,



and also of the quartary iodide,



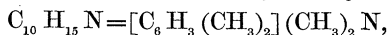
into which they were converted by the action of methyl iodide, and the platinum salts corresponding to these iodides,



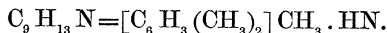
The two dimethylated toluidines here described obviously correspond to two of the three modifications of toluidine, and very probably to the two liquid modifications. Dimethyltoluidine, obtained by converting solid toluidine into the trimethylated toluylammonium iodide, and then submitting the corresponding hydrate to distillation, has a vol. w. 0.988, and boils at 210°. The substance thus obtained, the composition of which was likewise established by analysis of the platinum salt, essentially differs from the isomeric base boiling at 186°; it is less easily distinguished from the base boiling at 205°, with which more particularly it agrees in odour; in fact these two compounds exhibit only a slight difference of 5° in their boiling-points. Still I believe them to be isomeric, not identical.

It deserves to be noticed that while the boiling-point of solid toluidine (202°), by the introduction of two methyl groups, is raised by 8°, the boiling temperature of one of the liquid modifications (198°) is lowered by not less than 12°. Phenomena of this kind have been observed repeatedly in the course of this inquiry.

It has been already mentioned that, in addition to the two dimethylated toluidines, the product of the action of heat on trimethylated phenylammonium iodide contains methylxylidine. I have not been able to isolate this compound; but it was not difficult to prove its presence by the action of methyl iodide on the mixed bases. The two dimethylated toluidines are thus converted into quartary iodides; but, together with these compounds, there is formed a tertiary iodhydrate, the base of which is readily separated by distillation of the product with an alkali. The base thus liberated has the vol. w. 0.9293, and boils at 196°. Analysis of the platinum salt proved it to be dimethylated xyloidine,

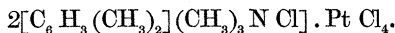


which previous to methylation must have obviously existed in the form of monomethylated xyloidine,



The presence of methylxylidine being only indirectly proved by analysis

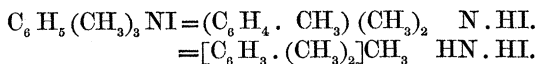
of the dimethylated base, it appeared desirable to establish the nature of the latter by additional experiments. For this purpose the tertiary monamine was converted, by means of methyl iodide, into the quaternary compound, the characters of which could not be mistaken, its composition being moreover established by analysis of the beautiful platinum salt,



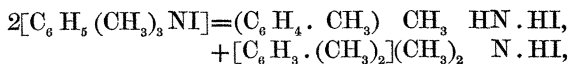
In performing these experiments I was astonished to observe how difficultly dimethylxylylidine combined with methyl iodide. Digestion at 100° produced no effect, and only by heating the mixture for many hours to a temperature of 150° combination took place, but even then only to a very small extent.

It was this indifference of dimethylxylylidine towards methyl iodide which enabled me to discover that small quantities of this compound are always formed, together with the monomethylated xylylidine, when trimethylated phenylammonium iodide is submitted to the action of heat. On treating the liquid, chiefly consisting of the two dimethylated toluidines and of monomethylated xylylidine, with methyl iodide, these bases, as I have pointed out, are converted into iodine compounds; the small quantity of dimethylxylylidine which as such exists in the liquid remains behind with the excess of methylic iodide, from which it may easily be separated by means of hydrochloric acid.

The formation of dimethylated toluidines and of monomethylated xylylidine requires no special explanation; it is due to intramolecular atomic interchange.



For the generation of dimethylxylylidine it is necessary to supply a methyl group from without. I have, however, already pointed out that, along with the principal transformation, several secondary reactions are taking place; those I hope to examine more minutely by-and-by. Dimethylxylylidine, which occurs in comparatively small quantity, obviously belongs to such a secondary change. The complementary product is probably monomethyltoluidine,



which I have not, however, as yet been able to trace.

Whilst engaged with these experiments, I have, for the sake of comparison, converted a specimen of xylylidine obtained from aniline-oil of high boiling-point into dimethylxylylidine. The xylylidine employed had a constant boiling-point at 216° . The tertiary base procured from it was observed to boil at 203° , *i. e.* 7° higher than the compound derived from trimethylated phenylammonium iodide; from this last derivative it differed, moreover, by combining much more readily with methyl iodide. The

quartary compound thus formed often remains liquid for days, and then suddenly solidifies into a beautiful mass of crystals.

Examination of the Monamines formed at High Temperatures.

It has been already stated that the bases into which trimethylated phenylammonium iodide is converted at very high temperatures (melting-point of lead) unmistakably exhibit the character of primary monamines. The only primary base which can arise from trimethylated phenylammonium iodide by intramolecular atomic interchange is a trimethylphenylated monamine, *i. e.* a cumidine.

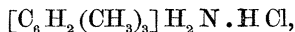


This, I may at once observe, is indeed the principal product of the reaction. It cannot, however, be wondered at that, under the influence of such extreme temperatures, many collateral changes must take place. The presence of by-products is at once perceived when the crystalline contents of the digestion-tube are submitted to distillation in a current of steam. Together with the vapour of water, a colourless oil is volatilized, consisting of hydrocarbons partly solid, partly liquid, the examination of which will form the subject of a future communication. Addition of an alkali to the liquid in the retort liberates considerable quantities of monamines, which, when dried over sodium hydrate, are observed to boil between 225° and 260°. By repeated distillation this range of boiling is still considerably expanded; at the same time, by far the largest portion of the liquid is found to pass between 217° and 230°. The primary nature not only of this main fraction, but also of the bases having both a lower and higher boiling-point, is at once manifested by the crystallizing power and insolubility of the salts which they produce. At whatever stage of the distillation a drop of the liquid passing be mixed with dilute hydrochloric or nitric acid, invariably splendid needles of chlorhydrates or nitrates are formed, the solutions of which, even when considerably diluted, solidify with platinum perchloride to double salts generally well crystallized. Another experiment rapidly indicating the primary character of these monamines may here be mentioned. On adding benzoyl chloride to the several basic fractions, much heat is evolved; and after cooling crystalline masses are produced, which are separated by water into soluble chlorhydrates and insoluble benzoyl compounds which may be crystallized from alcohol. None of the many secondary and tertiary monamines which have passed through my hands in the course of this inquiry exhibit this deportment; and accordingly benzoyl chloride may be recommended as a valuable reagent, readily applicable for primary bases. The method of recognizing primary monamines which I pointed out some time ago*, and which consists in converting them, by means of alcoholic

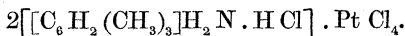
* Hofmann, D. chem. Berichte, 1870, p. 767.

potash and chloroform, into the powerfully smelling isonitriles, may also with advantage be resorted to.

The liquid boiling between 217° and 230° was separated by distillation into four fractions, each of which was then converted into a magnificently crystalline chlorhydrate. These several salts, after recrystallization, were all found to contain



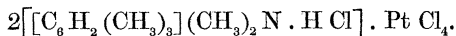
and to yield platinum salt of the composition



I was thus led to believe that the fraction boiling between 217° and 230° consisted of several isomeric cumidines; but on separating the bases from the several chlorhydrates, it was found that they all exhibited very nearly the same boiling-point. The liquid thus obtained boiled between 225° and 227° , and had the vol. w. 0.9633; it did not solidify when exposed to a temperature of -10° . I am therefore inclined to assume that only one cumidine is formed by the action of heat on trimethylated phenylammonium iodide, and that the irregularities in the boiling-point of the original fraction must be due to the presence of small quantities of impurities.

It deserves to be noticed that cumidine obtained from aniline, when heated with corrosive sublimate, yields no trace of red colouring-matter, whilst a splendid crimson is at once produced if a mixture of this base with pure aniline be treated. I reserve for a future communication the study of the colouring-matter thus obtained.

Taking into consideration the general observations recorded in the preceding paragraphs, the compound here designated as cumidine was naturally assumed to be a primary monamine. Little doubt as this conception appeared to present, it had nevertheless to be proved by experiment; for this purpose the base was submitted to methylation. Cumidine is readily acted upon by methylic iodide at the common temperature. Since it was only necessary to establish the degree of substitution, the first product of methylation was at once submitted to a second treatment; this second methylation likewise commenced at the common temperature, but had to be finished in the water-bath. The dimethylated base thus obtained had the vol. w. 0.9076: it boiled between 213° and 214° ; hence, in this case also, the insertion of two methyl groups had lowered the boiling-point. Dimethylcumidine may be cooled to -10° without solidifying: like all tertiary monamines, it forms very soluble salts, but gives a very beautiful platinum salt, containing



Remarkably enough, dimethylated cumidine exhibits the same reluctance to form a quaternary compound with methyl iodide that has already been pointed out as a peculiarity of the tertiary xylylidine. But whilst in the case of dimethylxylylidine, though difficultly and sparingly, combination after

all took place; all attempts with dimethylated cumidine have hitherto failed. The base was heated with methylic iodide for days in the water-bath, and ultimately even to 150° without any result. This inability of forming quartary compounds must, in one way or another, depend upon the arrangement of the material within the molecule. At all events, it deserves to be noticed that there are dimethylated xyloidines and cumidines which readily combine with methyl iodide. The dimethylated bases existing in the less volatile fractions of commercial dimethylaniline all form quartary compounds without difficulty, and must therefore correspond to xyloidines and cumidines which differ from those derived from trimethylated phenylammonium iodide.

In what relation stands the cumidine above described to the cumidines already known? Of the several purely methylic cumidines which are possible, two only are somewhat accurately known; these are the two bases which are derived, the one from so-called pseudocumol (obtained by treating xylylic bromide and methylic iodide with sodium), the other from mesitylöl. The former cumidine is a solid fusing at 62° , and need not therefore be further considered here. Most probably the cumidine above described will prove identical with the primary monamine corresponding to mesitylöl. Unfortunately mesitylamine has been hitherto so little studied, that even its boiling-point is not known. I hope next winter to examine more minutely this group of compounds.

In conclusion, I have great pleasure in expressing my best thanks to Mr. E. Mylius, Assistant in the Berlin Laboratory, for the zeal and care with which he has furthered the progress of these researches.

II. "Transformation of Aniline into Toluidine." By A. W. HOFMANN, M.D., Ph.D., F.R.S. Received August 22, 1872.

Whilst engaged with the experiments described in the previous paper, I have made some observations which I may be allowed briefly to mention to the Society, since the coming autumnal vacation will suspend work for a time.

In reviewing the experience collected as to the action of high temperatures upon trimethylated phenylammonium iodide, the question naturally suggested itself whether the transposition of methyl groups, such as it occurs in the quartary compound, would take place also on heating tertiary or secondary ammonium salts. Experiment has answered this question in the affirmative.

Generally speaking the phenomena are exactly what, from the results of former observations, might have been expected. It is my intention to study next winter more soundly the reactions here sketched out; for the present I may be permitted just to allude to the happy solution of a problem with which during the last few years I had repeatedly, but always unsuccessfully, been engaged.