

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 xylydines 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 xylydines 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 mesitylol. 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 mesitylol. 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.

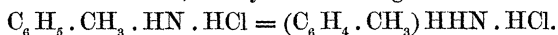
II. "Transformation of Aniline into Toluidine." By A. W. HOFMANN, M.D., Ph.D., F.R.S. Received August 22, 1872.

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.

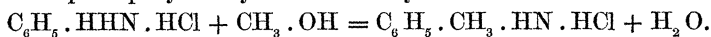
In reviewing the experience collected as to the action of high temperatures upon trimethylated phenylammonium iodide, the question naturally suggested itself whether the transposition of methyl groups, such as it occurs in the quartary compound, would take place also on heating tertiary or secondary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

Salts of methylaniline (experiments were made with the chlorhydrate and iodhydrate) may be heated to 220° or 230° for hours without undergoing any alteration; but if the temperature be raised to the melting-point of lead (335°), the methyl group in the ammonia fragment passes over to the benzol nucleus, methylaniline being converted into toluidine.

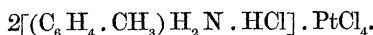


It is not necessary for this purpose to prepare methylaniline in the pure state. If a mixture of 1 molecule of pure aniline chlorhydrate and 1 molecule of methylic alcohol be heated for some hours to 230°–250°, a yellow transparent resinous mass of the consistency of honey is formed, which is principally methylaniline chlorhydrate.



After a day's exposure to a temperature of 335° the contents of the digestion-tubes are perfectly altered. In place of a transparent viscous resin, they now contain a solid beautifully crystalline mass; the secondary salt has been converted into a primary one. The crystalline mass, unless the temperature has been too high, dissolves in water almost without a residue; on addition of alkali to this solution an oily base is separated, which rises as a brownish layer to the surface of the liquid. If this oily layer be distilled in a current of steam, a colourless liquid passes, which, partly in the cooler, partly in the receiver, solidifies to a white crystalline mass of toluidine. There are but few secondary products formed in this reaction.

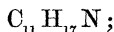
Toluidine thus obtained, when recrystallized from water, has the melting-point 45°. Though scarcely necessary, it was identified by a platinum determination, which gave the value corresponding to the formula



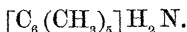
It deserves to be noticed that methylaniline iodhydrate, when heated like the chlorhydrate, yielded no solid, but liquid toluidine. I must leave it undecided which of the two liquid toluidines was formed in this case.

The observations rapidly sketched in this note invite to new experiments in a variety of directions. Is it possible to obtain by similar processes homologues of the monamines of other classes, perhaps even of some of the bases contained in the organism of plants and animals? Already I have commenced the study of naphthylamine, the behaviour of which will be particularly interesting in more than one respect. According to some observations published upon this subject, the preparation of methylated naphthylamines would appear to present some difficulty; but by working at moderate temperatures, mono- and dimethylated naphthylamine, as well as the quartary ammonium base, are readily procured. The salts of these compounds are remarkable for their power of crystallization; I have not yet found time to examine their behaviour under the influence of heat.

In conclusion I may observe also that the secondary products of the action of heat upon trimethylated phenylammonium iodide appear to be of interest. A small fraction of the bases, generated at 335° , boils at a very high temperature; when allowed to stand for some time this fraction deposits splendid crystals of a monamine which, according to the analysis of the well-crystallized chlorhydrate and platinum salt, contains



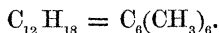
and the constitution of which, after a more minute examination, will probably prove to be expressed by the formula



Finally, there is found among these secondary products a beautifully crystallized hydrocarbon, melting at 136° , and boiling between 230° and 240° . Some combustions of this body, which require confirmation, lead to the simple formula



which determination of the gas volume weight will probably raise to



May this hydrocarbon actually be looked upon as sexmethylated benzol? If so, its oxidation promises results which will deserve minute investigation.

III. "Colouring-matters derived from Aromatic Azodiamines."

By A. W. HOFMANN, Ph.D., F.R.S., and A. GEYGER, Ph.D.
Received July 10, 1872.

II. *Safranine*.

Whilst we were engaged with the study of the blue colouring-matter produced by the action of aromatic monamines on azodiphenyldiamine our attention became directed to a beautiful red tar-pigment, which has been known for some time by the commercial name of *Safranine*, being extensively used as a substitute for safflower in dyeing silk and cotton. *Safranine* has not as yet been minutely examined; but, as far as can be judged from the scanty information we possess regarding its production, it is scarcely doubtful that this important dye must be looked upon as being the derivative of an azodiamine. The analysis of *safranine* thus promised to throw considerable light upon the nature of the compounds under examination.

The starting-point of our studies was the dye such as it occurs in commerce. The greater portion of it was supplied to us by Messrs. Tillmanns, of Crefeld. Another specimen was received from Dr. J. Wolf, and for a third one we are indebted to our friend M. Charles Girard, of Paris. Both the first-mentioned specimens were assigned to us as