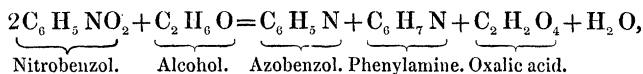VI. "Contributions towards the History of Azobenzol and Benzidine." By P. W. HOFMANN, Ph.D. Communicated by Dr. HOFMANN. Received July 24, 1860.

Among the numerous compounds into which benzol, when submitted to reagents, is converted, *azobenzol* and its derivatives have as yet received but limited attention. Although more than twenty-five years have elapsed since this interesting body was discovered by Mitscherlich, both its formation and its constitution remain still doubtful.

Mitscherlich [*], who discovered azobenzol in 1834, when submitting nitrobenzol to the action of an alcoholic solution of potassa, represented this compound by the formula

$$C_6 H_5 N [\dagger],$$
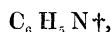
but left the reaction which gives rise to the formation of azobenzol unexplained. In 1845 this body was reprepared by Hofmann and Muspratt [‡], who observed among the collateral products of the reaction *aniline* and *oxalic acid*. They represent the formation of azobenzol by the equation

$$2\underbrace{C_6 H_5 NO_2}_{\text{Nitrobenzol.}} + \underbrace{C_2 H_6 O}_{\text{Alcohol.}} = \underbrace{C_6 H_5 N}_{\text{Azobenzol.}} + \underbrace{C_6 H_7 N}_{\text{Phenylamine.}} + \underbrace{C_2 H_2 O_4}_{\text{Oxalic acid.}} + H_2 O,$$

adding at the same time that they are far from considering this equation as more than the representation of *one* phase of the transformation of nitrobenzol, since several other rather indefinite compounds or products are formed simultaneously.

At about the same period Zinin made the interesting observation that azobenzol is capable of fixing hydrogen and of being thereby converted into a well-defined base, benzidine, which he represented by the formula

$$C_6 H_6 N.$$

Considering the physical characters both of azobenzol and of benzidine, especially the high boiling-points of these substances, and the ratio of hydrogen and nitrogen in the latter compound, the sum of
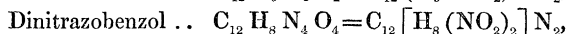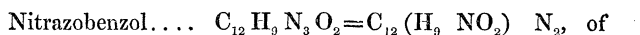
[*] Pogg. Ann. xxxii. p. 224.
[†] H = 1, O = 16, C = 12, &c.
[‡] Mem. of the Chem. Soc. vol. iii. p. 113.

the number of equivalents of these two elements not being divisible by 2, many chemists were inclined to double the formulæ of both bodies, and to represent them by the following expressions :—

$$\text{Azobenzol} \ldots \ldots \quad C_{12} H_{10} N_2$$
$$\text{Benzidine} \ldots \ldots \quad C_{12} H_{12} N_2$$

This view received the first experimental confirmation in the formation of the nitro-derivatives of azobenzol, which were examined in 1849 by Gerhardt and Laurent. The formation of

$$\text{Nitrazobenzol} \ldots \quad C_{12} H_9 N_3 O_2 = C_{12} (H_9 \quad NO_2) \quad N_2, \text{ of}$$
$$\text{Dinitrazobenzol} \ldots \quad C_{12} H_8 N_4 O_4 = C_{12} \left[H_8 (NO_2)_2 \right] N_2,$$

and of several derivatives of these bodies, having established the C_{12}-formula of azobenzol, but little doubt could be entertained regarding the formula of benzidine, which is as readily obtained from azobenzol by reducing agents, as it may be reconverted into azobenzol by nitric acid[*].

The molecular value of benzidine being thus almost exclusively fixed by the determination of the formula of the compound from which it originates, it was of some interest to obtain additional experimental evidence for the molecular weight of azobenzol.

With this view I have determined the vapour-density of azobenzol. This body boiling at a rather high temperature, I have availed myself of the method of displacement lately proposed by Professor Hofmann. Experiment proved the density of the azobenzol-vapour to be 94 referred to hydrogen as unity, or 6·50 referred to air. The theoretical vapour-density of azobenzol, assuming that one molecule of this compound furnishes, like the rest of well-examined substances, 2 vols. of vapour[†], is $\frac{182}{2} = 91$ referred to hydrogen, and 6·32 referred to air.

The determination of the vapour-density, then, plainly confirms the higher molecular weights proposed for azobenzol and for benzidine.

When determining the vapour-density of azobenzol, I had occasion to observe that, probably in consequence of a typographical error, the boiling-point of this compound is misstated in all the manuals which I could consult, and even in the original memoirs of Mitscherlich himself. The boiling-point is stated to be 193° C., whilst it is in reality 293° C.
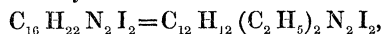
[*] Noble, Journal of the Chem. Soc. vol. viii. p. 293.　　[†] $H_2 O = 2$ vols.

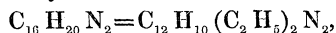Benzidine, when expressed by the formula
$$C_{12} H_{12} N_2,$$
presents itself as a well-defined diacid diamine. The molecular construction of the diatomic base remained to be decided.

I have endeavoured to solve this problem by the process of ethylation, as yet the simplest and the best guide in determining questions of this kind. Benzidine in the presence of alcohol is rapidly attacked by iodide of ethyl. After two hours' digestion at 100° C. in sealed tubes, the reaction is complete. The solution on evaporation yields a crystalline iodide,
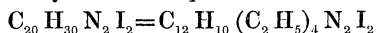$$C_{16} H_{22} N_2 I_2 = C_{12} H_{12} (C_2 H_5)_2 N_2 I_2,$$
from which ammonia separates a solid crystalline base very similar to benzidine. This compound, which fuses at 65° C., and resolidifies at 60° C., is *diethylbenzidine*:
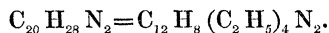$$C_{16} H_{20} N_2 = C_{12} H_{10} (C_2 H_5)_2 N_2,$$
which forms well-crystallizable salts with the acids, and yields with dichloride of platinum a difficultly soluble crystalline platinum-salt containing
$$C_{16} H_{22} N_2 Cl_2 \ 2PtCl_2.$$
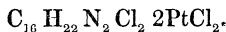
When diethylbenzidine is treated again with iodide of ethyl, the phenomena previously observed repeat themselves. The iodide
$$C_{20} H_{30} N_2 I_2 = C_{12} H_{10} (C_2 H_5)_4 N_2 I_2$$
is formed, which when decomposed by ammonia yields *tetrethylbenzidine*
$$C_{20} H_{28} N_2 = C_{12} H_8 (C_2 H_5)_4 N_2.$$
Tetrethylbenzidine resembles the diethylated and the non-ethylated base. It fuses at 85° C., resolidifying at 80° C., produces with the acids crystalline compounds, and furnishes with dichloride of platinum a platinum-salt of the formula
$$C_{20} H_{30} N_2 Cl_2, \ 2PtCl_2.$$
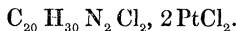
The further action of iodide of ethyl upon tetrethylbenzidine is extremely slow. After 12 hours' digestion at 100° C. only a very minute quantity of the base had been transformed into an iodide. Iodide of methyl, on the other hand, acts with great energy. An hour's digestion is sufficient to produce the final diammonium-compound.
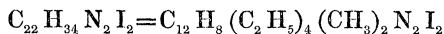
The iodide
$$C_{22} H_{34} N_2 I_2 = C_{12} H_8 (C_2 H_5)_4 (CH_3)_2 N_2 I_2$$
is very difficultly soluble in absolute alcohol, but dissolves with facility in boiling water, from which it is deposited on cooling, in

long beautiful needles. The solution of this iodide is no longer pre-
cipitated by ammonia, but yields with oxide of silver a powerfully
alkaline solution, exhibiting all the characters of the completely sub-
stituted ammonium- and diammonium-bases discovered by Professor
Hofmann. The solution of this dimethyl-tetrethylated base, which
contains

$$C_{22} H_{36} N_2 O_2 = \left. \begin{matrix} C_{12} H_8 (C_2 H_5)_4 (CH_3)_2 N_2 \\ H_2 \end{matrix} \right\} O_2,$$
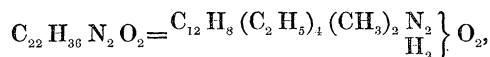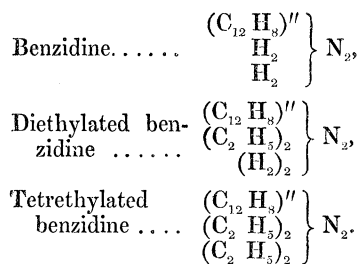
is not further acted upon by either iodide of ethyl or methyl.
With acids it forms a series of salts which are remarkable for the
beauty with which they crystallize. The platinum-salt is almost in-
soluble in water, but soluble with difficulty in concentrated boiling
hydrochloric acid, crystallizing from this solution on cooling in
beautiful needles. This salt contains
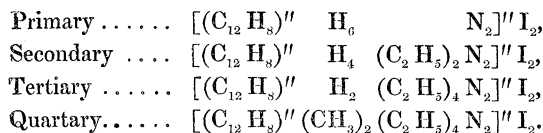
$$C_{22} H_{34} N_2 Cl_2, 2 PtCl_2.$$
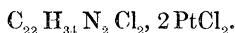
The above experiments appear to establish the molecular construction
of benzidine in a satisfactory manner. This base is obviously a
primary diamine, in which the molecular group $C_{12} H_8$, whatever its
nature may be, functions as a diatomic radical. A glance at the
subjoined Table exhibits the construction of benzidine and of the
several compounds which I have described.

Diamines.

$$\text{Benzidine......} \quad \left. \begin{matrix} (C_{12} H_8)'' \\ H_2 \\ H_2 \end{matrix} \right\} N_2,$$

$$\begin{matrix} \text{Diethylated ben-} \\ \text{zidine ......} \end{matrix} \quad \left. \begin{matrix} (C_{12} H_8)'' \\ (C_2 H_5)_2 \\ (H_2)_2 \end{matrix} \right\} N_2,$$

$$\begin{matrix} \text{Tetrethylated} \\ \text{benzidine ....} \end{matrix} \quad \left. \begin{matrix} (C_{12} H_8)'' \\ (C_2 H_5)_2 \\ (C_2 H_5)_2 \end{matrix} \right\} N_2.$$

Iodides of Diammoniums.

$$\text{Primary......} \quad [(C_{12} H_8)'' \quad H_6 \qquad\qquad N_2]'' I_2,$$
$$\text{Secondary ....} \quad [(C_{12} H_8)'' \quad H_4 \quad (C_2 H_5)_2 N_2]'' I_2,$$
$$\text{Tertiary ......} \quad [(C_{12} H_8)'' \quad H_2 \quad (C_2 H_5)_4 N_2]'' I_2,$$
$$\text{Quartary......} \quad [(C_{12} H_8)'' (CH_3)_2 (C_2 H_5)_4 N_2]'' I_2.$$

The experiments described in this note were performed in Pro-
fessor Hofmann's laboratory.