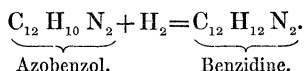


V. "Notes of Researches on the Polyammonias, No. XXIII.—
Hydrazobenzol, a new Compound isomeric with Benzidine."
By A. W. HOFMANN, LL.D., F.R.S., &c. Received May 7,
1863.

The discovery, among the secondary products of the manufacture of aniline, of xenylamine, the probable connexion of which with benzidine (xenylene-diamine) I have already had an opportunity of pointing out*, has induced me to submit the latter compound to some experiments. In preparing benzidine by the process originally pointed out by Zinin†, viz. by treatment of azobenzol with sulphide of ammonium, I was led to the observation of some phenomena which appear to have escaped the attention of those who have hitherto studied this substance.

It is generally supposed that the action of reducing agents upon azobenzol produces directly benzidine.



Such, however, is not the case. The well-defined base designated by the latter name is only a secondary product; the first compound which is generated in this process being a neutral or feebly basic body, differing in all its properties from benzidine, with which, however, it is isomeric, and into which it may be converted by simple treatment with strong mineral acids.

On passing a current of sulphuretted hydrogen into a solution of azobenzol in alcoholic ammonia, the yellowish-red liquid is rapidly decolorized, and yields on addition of water a crystalline precipitate of a peculiar camphor-like smell. This substance contains a minute quantity of the sulphur which separates, the bulk of which, however, remains dissolved as polysulphide of ammonium; it is easily purified by two or three crystallizations from very dilute alcohol. Submitted to combustion, the compound thus obtained yields numbers which coincide with those furnished by the analysis of benzidine.

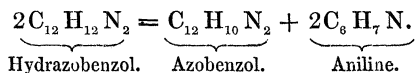
The properties in which the new substance, for which I propose the name *hydrazobenzol*, differs from benzidine are the following:—*Hydrazobenzol* crystallizes from alcohol, and more especially from

* Proc. Roy. Soc. vol. xii. p. 389.

† Journ. Prakt. Chem. vol. xxvi. p. 93.

benzol (in which it is somewhat less soluble), in well-developed white plates, benzidine being always deposited from these solvents in well-defined needles; and whilst the latter is freely soluble in boiling water, from which it separates on cooling in the form of a crystalline mass of nacreous lustre, the former is so sparingly soluble in water that it is impossible to recrystallize it from that solvent. The fusing-point of hydrazobenzol is 131°C ., that of benzidine being 118°C . The basic properties of benzidine are well defined; it dissolves even in the weakest acids, such as acetic acid, in which hydrazobenzol is nearly insoluble. Stronger acids, such as hydrochloric and sulphuric acids, more especially on application of heat, dissolve hydrazobenzol; but the solution thus obtained contains no longer the unchanged body; the addition of alkali, fixed or volatile, produces a precipitate which now possesses all the properties of *benzidine*.

These characters are sufficient to individualize hydrazobenzol. There is, however, another property which marks its difference from benzidine in even a more conspicuous manner. Benzidine when submitted to a high temperature distils; a certain portion is decomposed in this process, but the larger quantity is volatilized without decomposition. On heating hydrazobenzol considerably above its fusing-point, a powerful reaction ensues, the heat evolved being sufficient to carry over nearly the whole amount of substance in the form of a deep red oil, from which, on cooling, crystals of azobenzol are deposited. On addition of an acid the oil yields a further quantity of this substance, and the acid solution is then found to contain abundance of aniline. The reaction which occurs is simple enough.



I had hoped that among the products of the reaction paraniline ($\text{C}_{12}\text{H}_{14}\text{N}_2 = 2\text{C}_6\text{H}_7\text{N}$) might be met with; in this hope I have been disappointed.

The reproduction of azobenzol from hydrazobenzol may be accomplished in a variety of other ways. Nitrous acid, chlorine, bromine, iodine, chromate and permanganate of potassium, and nitrate of silver produce this effect in a most easy manner; in these processes the loosely adherent hydrogen is simply eliminated, no aniline being formed as a secondary product. Even when moistened with alcohol

and exposed to the action of the atmosphere, hydrazobenzol is gradually reconverted into azobenzol.

It deserves to be noticed that some of the chemists who have been engaged in the examination of benzidine must have occasionally worked with hydrazobenzol. Mr. Noble*, who many years ago prepared benzidine in my laboratory, especially remarks that the substance obtained by him is reconverted into azobenzol by the action of nitrous acid. I have satisfied myself that benzidine thus treated yields no trace of azobenzol.

From the experiments described, it is obvious that in the formation of benzidine from azobenzol two distinct phases have to be distinguished: in the first phase the molecule of azobenzol assimilates a molecule of hydrogen, but this hydrogen remains in a very feeble state of combination, being eliminated again by a great variety of agents. It is only under the influence of acids that the hydrogen molecule becomes incorporated in the system, if I may use this expression, and fixed benzidine, a substance of great stability, is formed.

Whatever view may be taken regarding the nature of azobenzol, the constitution of which it must be admitted is utterly unknown, the intermediate substance has to be viewed as its hydrogen compound, and it is this consideration which induced me to propose the name *hydrazobenzol*.

VI. "Note on the Composition of Aniline-Blue." By A. W. HOFMANN, LL.D., F.R.S., &c. Received May 21, 1863.

The prosecution of my researches on the aniline colours has led me to a result of great simplicity, which I hasten to lay before the Royal Society.

Aniline-blue is triphenylic rosaniline.

Aniline-red, Rosaniline $C_{20}H_{19}N_3, H_2O$.

Aniline-blue, Triphenylic Rosaniline $C_{20}H_{18}N_3, H_2O$.
 $(C_6H_5)_3$.

The commercial article is a salt of the base, the hydrochlorate for example, the composition of which corresponds to the monatomic hydrochlorate of rosaniline.

* Chem. Soc. Quart. Journ. vol. viii. p. 292.