

# Formation of Triphenylpararosaniline Hydrochloride from Diphenylamine and Chloralammonia

By

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About 14 years ago M. Kuhara obtained a blue-coloured substance by heating diphenylamine and chloralammonia in a vacuum, and S. Idesaki<sup>1</sup> working under his direction confirmed experimentally that the blue compound is triphenylpararosaniline hydrochloride. The question of the mechanism of the formation having been left hitherto unsolved the author took up the problem and investigated how the reaction progresses.

## **I. Preparation of the blue compound and its properties**

The blue compound was prepared according to Idesaki's description as follows: Diphenylamine and chloralammonia were mixed together in a molecular proportion and heated on a water bath for about one hour. By this treatment ammonia was evolved, but the diphenylamine was observed to remain practically unchanged. The mixture was then heated with direct fire at 130° C under a reduced or ordinary pressure, when it melted and then boiled. On continuing the boiling a sudden change of colour from green to blue took place and at the same time hydrogen chloride gas was evolved. The dark-coloured mass obtained on cooling was washed first with hot benzene

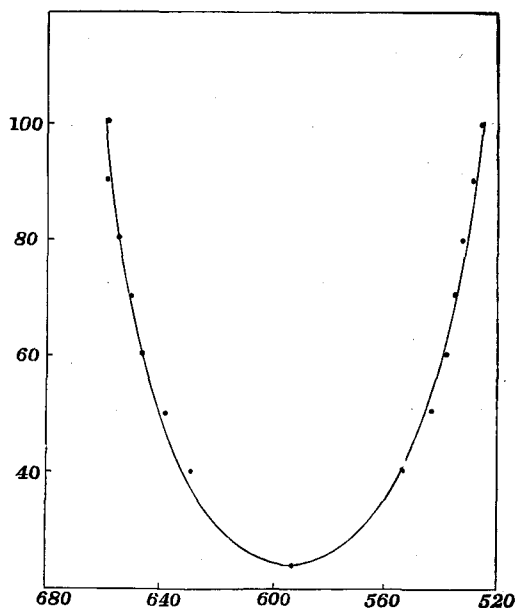
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and then with ether to remove the diphenylamine left unchanged, and treated with hot alcohol in which the blue compound readily dissolved. A concentrated hydrochloric acid was added to the alcoholic extract and the mixture left to stand for several hours, and later the blue precipitates formed were filtered. This process of precipitation was repeated several times, and finally the precipitates were washed with chloroform and recrystallized from alcohol or from aniline on addition of ether.

The substance thus purified was obtained as a crystalline powder with golden lustre as stated by Baeyer and Villiger,<sup>1</sup> and the brilliant blue colour of its alcoholic solution was seen to turn to reddish brown on addition of alcoholic sodium hydroxide, which shows that the corresponding free base, triphenylpararosaniline was thus formed. All its properties were found to agree exactly with those of triphenylpararosaniline hydrochloride. The absorption spectrum of its alcoholic solution showed only one absorption band whose maximum lies nearly at  $593 \mu\mu$ , as may be seen in the following figure:

Fig. 1.



This fact agrees fairly well with the observation of Formánek.<sup>2</sup>

<sup>1</sup> Ber. D. Chem. Ges., 37, 2872 (1904).

<sup>2</sup> Formánek: Untersuchung und Nachweis org. Farbstoffe auf spectroscop. Wege.

## II. Mechanism of the Reaction

In the preparation of the blue compound above described the previous heating of the mixture on a water bath is necessary, otherwise the yield becomes so poor that it can hardly be separated. If however chloral ammonia heated once on a water bath be used, we can apply direct fire at once without the fear of lessening the yield. From this fact it is clearly to be seen that what takes part in the formation of the blue compound is not chloral ammonia itself, but its decomposition products.

Now chloral ammonia is known to undergo decomposition at 100° and to give the following substances as decomposition products:<sup>1</sup>

Chloroform.

Formamide.

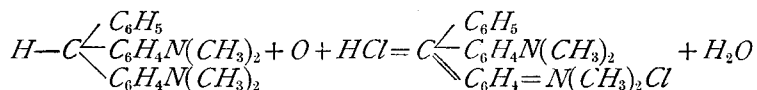
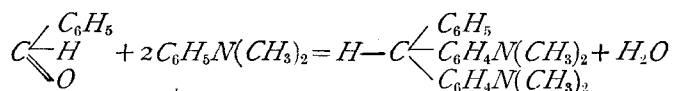
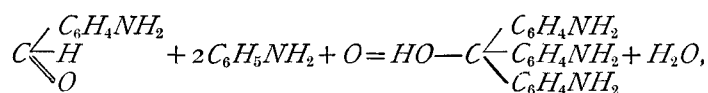
Chloralimide.

Isochloralimide

Chloraldiformamide.

It is therefore to be decided which of these substances interacts with diphenylamine and produces the diphenylamine blue.

Looking at the general modes of formation of the dyestuffs belonging to the triphenylmethane series, we perceive that the carbon in the CHO group often becomes the central carbon atom of the dyestuffs thus :



But it is to be noted that all these reactions are only brought about

<sup>1</sup> Personne: Lieb. Ann., 157, 114 (1871), Béhal et Choay: Ann. chim. phys. [6] 26, 5 (1892); 27, 319 (1892).

by aid of some oxidizing agent, without which the leucocompound first formed can not be further transformed into the coloured compound.<sup>1</sup>

Since there is no oxidising agent among the decomposition products of chloralammonia it seems impossible to regard the carbon in the aldehyde group as the source of the central carbon atom of the diphenylamine blue in this experiment. If this be admitted there is only one alternative, that is the central carbon in the diphenylamine blue can only be regarded as originating from the carbon in the trichloromethyl radical.

As to the reactions between the compounds containing the  $\text{CCl}_3$  group and the aromatic amines not a few are mentioned in chemical literature. Girard and de Laire prepared diphenylamine blue from diphenylamine and perchloroethane, Döbner<sup>2</sup> obtained malachite green from dimethylaniline and benzotrachloride, and Hofmann prepared magenta by treating aniline with carbon tetrachloride. Some of these reactions take place only in the presence of a catalyser, but in no case is an oxidizing agent needed.

To confirm the above contention experimentally the behaviour of diphenylamine toward the compounds containing the aldehyde group on the one hand and toward those having the  $\text{CCl}_3$  group on the other, was investigated. As the substance containing the aldehyde group, formic acid, acetaldehyde, formamide, formylphenylhydrazine and formanilide were selected, and each was heated with diphenylamine. All these experiments gave no satisfactory result the blue compound was obtained in not one instance. Formaldehyde<sup>3</sup> is known to act upon diphenylamine and to produce diphenylamine blue. But even with this some oxidising agent is needed, without which the reaction never progresses so as to produce diphenylamine blue. Next to know the behaviour of compounds containing the  $\text{CCl}_3$  group carbon tetrachloride, chloroform, chloral, trichloroacetic acid, chloralimide, isochloralimide, and chloraldiformamide were taken, and their action toward diphenylamine was studied. In this case diphenylamine blue was always produced, the only exception having been the action of chloroform which ended in the formation of the leucocompound.

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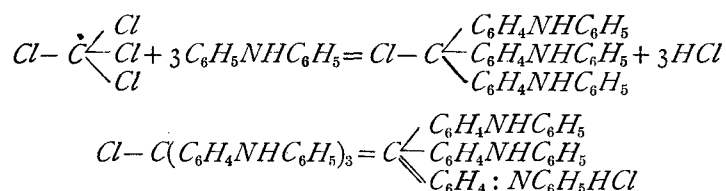
<sup>1</sup> Hofmann: *Lieb. Ann.*, 132, 296 (1864), O. Fischer: *Ber. D. Chem. Ges.* 10, 1625 (1877).

<sup>2</sup> *Ber. D. Chem. Ges.*, 11, 1238 (1878).

<sup>3</sup> *Farbw. Meister, Lucius and Brüning*: *Chem. Centralb.*, 1893, I, 1103.

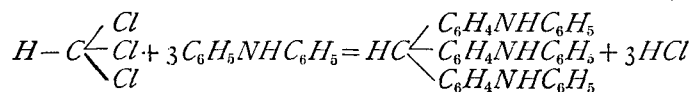
a. Carbontetrachloride and Diphenylamine

A mixture of carbon tetrachloride and diphenylamine, with some zinc chloride added, was heated at 130° when the formation of the blue compound quickly took place, followed by the evolution of hydrogen chloride. Some reddish-coloured compound was produced as the by-product from which diphenylamine blue could easily be separated, as the former is more soluble in alcohol. The reaction may be represented as follows :



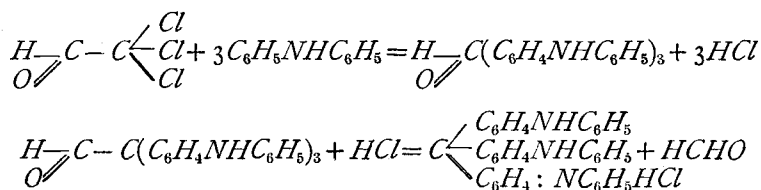
b. Chloroform and Diphenylamine

Diphenylamine was heated with chloroform in the presence of zinc chloride. No colour change took place. The addition of an oxidising agent such as arsenic acid, however, quickly brought about the change. It is therefore very clear that the leuco-compound of diphenylamine blue was formed by their interaction thus :



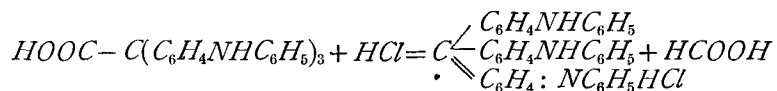
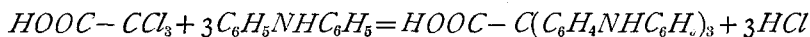
c. Chloral and Diphenylamine

When chloral was heated with diphenylamine the formation of the blue was accompanied with the evolution of gas which was proved to consist of a mixture of hydrogen chloride and formaldehyde. Judging from this fact the representation of the reaction by the following scheme seems probable.

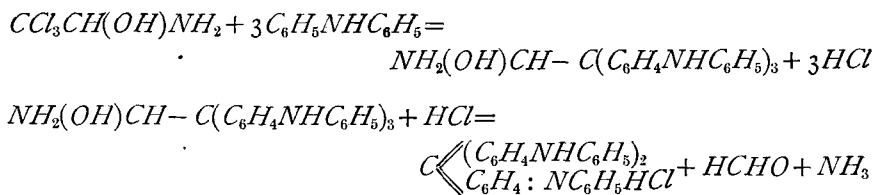


*d. Trichloroacetic acid and Diphenylamine*

The reaction between trichloroacetic acid and diphenylamine took place easily and diphenylamine blue was produced. In the gas evolved in the reaction the presence of formic acid was confirmed.

*e. Chloral ammonia and Diphenylamine*

As was described before chloral ammonia and diphenylamine react together at 130° to form triphenylpararosaniline hydrochloride, though the yield is very scant. The reaction may be represented as follows:



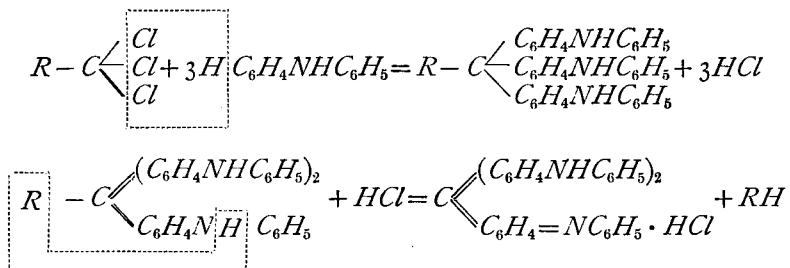
In like manner chloralimide, isochloralimide and chloraldiformamide were all found to react with diphenylamine so as to produce diphenylamine blue as the reaction product.

**III. Conclusion**

1. When heated directly at 130° diphenylamine and chloral ammonia produce only a small quantity of triphenylpararosaniline hydrochloride; if the mixture is heated at 100° for some time and then the temperature raised to 130° the yield of the dyestuff is greatly increased.

2. In order to seek for the cause of the reaction the interaction between diphenylamine and each of the decomposition products produced from chloral ammonia at 100° was studied, and a generalization was attained as follows: that the compounds which take part in the formation of diphenylamine blue are those containing the CCl<sub>3</sub> group but not the CHO group.

3. To explain the mechanism of the reaction the author put forward an assumption that the chlorine atoms in the  $\text{CCl}_3$  group are replaced by the phenyl group, and the substance thus produced further changes in the dyestuff by the action of hydrogen chloride as is shown by the following equation :



The author wishes to express his sincere thanks to the late Prof. M. Kuhara under whose direction this work was carried out.