method of treatment of a medicinal preparation containing these substances is then outlined, and the success obtained in their identification pointed out.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO.]

NITROSO-TRIPHENYLAMINE AND COLORS OF THE SECOND ORDER.

BY JEAN PICCARD AND MORRIS KHARASCH.[1]

Received March 25, 1918.

Theoretical Part.

It is a well-known rule[2] that the color of a yellow dye changes with increase of molecular weight to orange, red, violet, blue, and finally to green. Each one of these colors is called lower than the preceding one, and higher than the following one. Generally, we can lower the color by the introduction of alkyl or aryl radicles into the auxochromic or chromophoric groups of the dye.

The spectroscopic explanation of this behavior of dyes is that a yellow dye has an absorption band in the violet, and any increase in the molecular weight decreases the number of vibrations corresponding to this absorption band causing the band to shift toward the red end of the spectrum. When the absorption band is in the blue the compound appears orange, and as the absorption band goes through green, yellow, orange to red, the color of the respective compounds successively changes to red, violet, blue, and green. A compound has the color complementary to that of its maximum absorption. On the other hand, if in the molecule of a yellow dye we make such changes as generally tend to produce a higher color, then the absorption bands shift into the ultra-violet part of the spectrum, the compound becoming colorless.

Absorption colors have very much in common with interference colors. The colors of Newton, for instance, are also produced by an absorption band going through the spectrum in the same direction in which the absorption bands of chemical compounds shift with increase of molecular weight. Thin layers of any oil, soap bubbles and glass, are first yellow in reflected light, and as the thickness of the layer increases, the color becomes orange, red, violet, blue and green. The last color has an absorption band in the red, but in the violet end of the spectrum there appears a new band. If the layer becomes still thicker, the first band (in the red) shifts into the ultra red, and we have only the second band, which is in the violet. Our layer is now again yellow but yellow of the second order.

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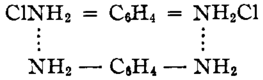
[1] A part of this work was done in collaboration with E. H. Fleck.

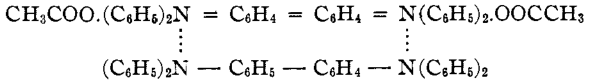
[2] Nietzki, *Verh. des Vereins zur Förderung des Gewerbefleisses*, 58, 231 (1879).

Some years ago one of us became interested in what would happen if a dye with a lower color than green were prepared. The number of green dyes is relatively small, and most of them have already so many alkyl and aryl radicles in their auxochrome and chromophore groups that any further increase in molecular weight is almost impossible. In the field of meriquinoid dyes an opportunity for such experiments was found. These dyes begin with yellow (meriquinone di-immonium salts)



$$\begin{array}{c} \mathrm{ClNH_2 = C_6H_4 = NH_2Cl} \\ \vdots \qquad\qquad\quad \vdots \\ \mathrm{NH_2 - C_6H_4 - NH_2} \end{array}$$

and go to green (meri-tetramethyldiphenoquinone-di-immonium salt). When we substituted 8 phenyl groups for the 8 methyls in the last named green compound, a substitution which always lowers the color, a new yellow dye was obtained which was the first representative of absorption colors of second order, namely,



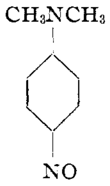
$$\begin{array}{c} \mathrm{CH_3COO.(C_6H_5)_2N = C_6H_4 = C_6H_4 = N(C_6H_5)_2.OOCCH_3} \\ \vdots \qquad\qquad\qquad\qquad\qquad\qquad \vdots \\ \mathrm{(C_6H_5)_2N - C_6H_5 - C_6H_4 - N(C_6H_5)_2} \end{array}$$

meri-tetraphenyl-diphenoquinone-di-immonium acetate.

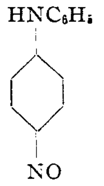
The above mentioned experiments demonstrate that the rule for interference colors of second order holds good in case of absorption colors. The first absorption band, or group of absorption bands, is always followed by a second one which corresponds approximately to double the number of vibrations of the first one; it is the octave of the first.

Since the paper of Piccard[1] was published attention has been called to a few more examples of colors of the second order, but none of them gives a much lower color than yellowish green, or greenish yellow. The new theory led, however, to such encouraging results, in explaining the colors of new compounds, that we have tried to go one step further, to prepare an orange compound of the second order. We have chosen the group of *p*-nitrosoanilines for this work.

In the *p*-nitrosoanilines the dimethyl compound is already yellowish green. The monophenyl (*p*-nitroso-diphenylamine) is greenish yellow in benzene solution, while in alcohol it is orange.[2]



Green.



Greenish yellow.

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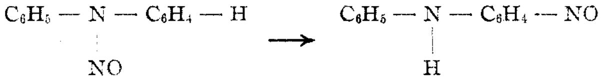
[1] Jean Piccard, *Ber.*, 46, 1843 (1913).

[2] There is very little doubt as to the fact that the alcoholic solution of the *p*-nitrosodiphenylamine contains an addition compound. See F. Strauss and Zeime, *Ber.*, 46, 2267 (1913).

To complete the above given group of dyes, and to compare their colors, it was necessary to have the diphenyl-nitrosoaniline (nitroso-triphenylamine). We were puzzled by the fact that nitroso-triphenylamine, which is very interesting from a purely chemical point of view, had not as yet been prepared, and it was not without apprehension that we began this work. In the literature we found mention of several vain attempts to prepare this compound, It seemed, from all the work done, as if in triphenylamine the nitrogen had lost all influence on the rest of the molecule, the *p*-hydrogen atoms behaving like the hydrogen in benzene. The nitro compound is easily formed, but nitrous acid does not give a nitroso derivative. If any action took place at all, the only isolated product of the reaction was the *p*-nitroso-triphenylamine. On the other hand, we know from the work of Wieland that triphenylamine gives on oxidation derivatives of tetraphenylbenzidine.

After experimenting for some time and obtaining only the previously mentioned derivatives, we finally succeeded in working out a method for the preparation of nitroso-triphenylamine. While working out this method, we were influenced by the following considerations. In the well-known Fisher-Hepp reaction, the parahydrogen changes place with the —NO of the nitrosamine group.



$$C_6H_5-\underset{\substack{|\\ NO}}{N}-C_6H_4-H \longrightarrow C_6H_5-\underset{\substack{|\\ H}}{N}-C_6H_4-NO$$

We thought that it might not be essential that the —NO group should be in the same molecule as the hydrogen. So we tried to duplicate the conditions of the Fisher-Hepp reaction as well as we could, except that the —NO group was attached to another molecule, by using amyl nitrite.

$$(C_6H_5)_2N-C_6H_4-H+C_5H_{11}O-NO \longrightarrow (C_6H_5)_2N-C_6H_4-NO+C_5H_{11}O-H.$$

Experimentally this was carried out by treating a suspension of triphenylamine in absolute alcohol, saturated with hydrogen chloride, with amylnitrite at —5°. In this way we obtained the nitroso compound, the yield being nearly quantitative with respect both to the triphenylamine and the amylnitrite.

The new compound was to our surprise a chloride which could easily be recrystallized from methyl alcohol. The chloride is without doubt $Cl(C_6H_5)_2N:C_6H_4:NOH$ (diphenyl-quinone-monimine-oxime chloride),[1] triphenylamine having no affinity for HCl.

Nitroso-triphenylamine was easily prepared by the hydrolysis of this salt with water.

The color of the base and the chloride are alike, but we must not forget

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[1] We shall use the abbreviation nitroso-triphenylamine hydrochloride hereafter in referring to this compound.

that the former is orange of the second order, and the latter orange of the first order. The colors of the chlorides of nitroso-anilines begin with light yellow, and are very slightly lowered by the introduction of methyl groups. Even the monophenyl derivative is only orange-yellow. So we could not expect a much lower color than orange-yellow for a diphenyl derivative.

On the other hand the color of the free bases begins with green and goes to greenish yellow (nitroso-diphenylamine). For the next member we must expect a still lower color.

The nitroso group of the nitroso-triphenylamine is in the para position. This was proved by reducing the nitroso-triphenylamine with zinc and acetic acid to the amino compound. This in turn was converted with acetyl chloride into the acetyl derivative, which was found to be identical with that prepared by Herz from *p*-nitrotriphenylamine.[1]

Experimental Part.

The Preparation of Triphenylamine.—The following modified method of Irma Goldberg and Marie Nimerovsky[2] for preparing triphenylamine gave very satisfactory results: A mixture of 116 g. of diphenylamine, 140 g. of phenyliodide, 72 g. of potassium carbonate (1.5 times the theoretical quantity) 2.5 g. of catalytic copper[3] and 300 cc. of nitrobenzene, was heated for 12 hours at 207°[4] in a copper flask, fitted with an air condenser. The brown-colored solution was then subjected to steam distillation, whereby the nitrobenzene and the excess of phenyliodide were separated from the products of the reaction. Benzene was added to the mixture of di- and triphenylamines, potassium iodide and copper and the whole filtered through glass wool, to free it from copper. The benzene solution was then separated from the water, dried with anhydrous sodium sulfate, and the benzene distilled off. The crude product (157 g.) was dissolved in hot glacial acetic acid. Upon cooling, the triphenylamine crystallized out (120 g., m. p., 124.5°). When recrystallized from methyl alcohol the triphenylamine was obtained in small almost colorless crystals, melting at 127°.

Nitroso-triphenylamine Hydrochloride.—Twenty g. of triphenylamine was dissolved in 170 cc. of hot absolute alcohol, the solution cooled rapidly and the resulting suspension treated with 300 cc. of a solution of alcohol saturated with hydrogen chloride. Dry hydrogen chloride was then passed through the suspension, and amyl nitrite slowly added, the whole being well cooled (—5°) and constantly shaken during the operation. The solution first turned blue, and, as more amyl nitrite was added, red. The end of the reaction was ascertained by diluting a drop of the solution with water,

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[1] THIS JOURNAL, **39**, 2006 (1917); also *Ber.*, 40, 2451 (1907).

[2] *Ber.*, **40**, 2451 (1907).

[3] THIS JOURNAL, **39**, 2006 (1917).

[4] The temperature is that of the oil bath in which the copper flask was immersed.

and testing with potassium iodide-starch paper. The solution was allowed to stand for 2 hours longer at —20°, while a slow stream of dry hydrogen chloride was passed through it. An orange-red to carmine product separated out, the color depending on the quantity of hydrogen chloride introduced. This, the hydrochloride of nitroso-triphenylamine, was filtered off and washed with absolute alcohol. The yield is very good (20 g.).

It is important to note that sometimes smaller or greater quantities of the nitrotriphenylamine are formed along with the nitroso compound, this depending entirely on the quality of the amyl nitrite used. For purification the nitrosotriphenylamine hydrochloride thus obtained was first converted into the free base, by suspending the hydrochloride in cold water for 2 hours. It was then filtered, washed with cold water until a sample of the washings gave no precipitate with silver nitrate, and dried in a vacuum desiccator. When absolutely dry, the free base was dissolved in ether (dried over calcium chloride) and its hydrochloride precipitated by dry hydrogen chloride. The nitrotriphenylamine remained in solution. The hydrochloride when recrystallized[1] from methyl alcohol (1 g. in 30 cc.) was obtained in long, brown needles melting at 178°.

The chlorine was determined by addition of $AgNO_3$ to the water extract of the hydrochloride.

Subst., 0.5000; AgCl., 0.2283.
Calc. for $C_{18}H_{15}N_2OCl$: Cl, 11.42. Found: 11.30.

***p*-Nitroso-triphenylamine.**—The free base, obtained by hydrolysis of the pure hydrochloride, was recrystallized twice from methyl alcohol, giving beautiful, long, brown needles, melting at 120.5° (corr.). The powdered substance is orange.

Subst., 0.1268, 0.1012; CO_2, 0.3660, 0.2923; H_2O, 0.0602, 0.0473, 0.2295, 0.1327; 21.20, 12.40 cc. dry N_2 at 20°, 24° and 735.5, 735.5 mm.

Calc. for $C_{18}H_{14}N_2O$: C, 78.83; H, 5.15; N, 10.27. Found: C, 78.70, 78.76; H, 5.27, 5.19; N, 10.42, 10.40.

The nitroso-triphenylamine is soluble in methyl alcohol (1 g. per 30 cc. of the boiling alcohol), more so in ethyl alcohol, and very easily in ether and benzene. In an excess of dil. sulfuric or hydrochloric acid the nitroso-triphenylamine dissolves with a red color, and is not precipitated by the addition of water. An acetic acid solution of the base has the color of bromine.

Summary.

1. It is possible—under certain conditions—to introduce a nitroso group into the molecule of triphenylamine.
2. The nitroso-triphenylamine so formed is a para compound.
3. The color of *p*-nitroso-triphenylamine is orange of the second order.

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[1] The yield was better if after cooling at —20° we introduced dry HCl gas into the solution.

The following table shows the colors of the different *p*-nitroso-anilines:

	Color.				
Formula.	Salt.	Base.	In benzene sol.	In alcohol sol.	In alcohol water sol.
$C_6H_5.NO$[1].	. . .	blue-green (melted)	blue-green	blue-green	. .
$H_2N.C_6H_4.NO$.	yellow	yellowish green	. . . . .[2]	. . . . .	. . .
$(CH_3)_2N.C_6H_4.NO$.	yellow	yellowish green	yellowish green	greenish yellow	yellow
$(C_6H_5)HNC_6H_4.NO$.	orange-brown	orange	greenish yellow	yellowish orange	orange
$(C_6H_5)_2.N.C_6H_4.NO$.	orange-brown	orange	yellow	orange	orange-red

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO.]

THE OXIDATION OF DIAMINOPHENOLS.

BY JEAN PICCARD AND LOUIS M. LARSEN.[3]

Received March 25, 1918.

Theoretical Part.

That diaminophenols on oxidation give red solutions is known to all who have worked with these substances. F. Kehrmann and H. Prager[4] succeeded in isolating some of these oxidation products and recognized them as salts of holoquinoid[5] aminoquinonimines. Some years later, Jean Piccard[6] re-investigated these compounds; by titration and by reduction to the original leucobase he confirmed the formulas given by Kehrmann and Prager. On the other hand, he compared the absorption spectra with those of the meriquinoid salts,[3] selecting such representatives as the

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[1] We indicate here the color of nitroso-benzene, although, strictly speaking it does not belong to the same family.

[2] We do not know why this mother-substance is much less soluble than the other members of the group. It is probably in connection with this phenomenon that the solutions of this compound are more yellowish than those of the dimethyl derivatives.

[3] A part of this work was done by one of us in the Chemical Laboratory of the Royal Academy of Sciences in Munich in 1912 but has not previously been published.

[4] *Ber.*, **39**, 3438 (1906).

[5] Holoquinoid is applied to those aromatic compounds which possess the quinoid structure. Quinone, $O = C_6H_4 = O$, is a common example. Meriquinoid is applied to those quinonimine salts, whose C_6 rings are (as in quinhydrone) partly quinoid and partly hydroquinoid. Red of Wurster and magenta, shown above, are examples of this class. They have always a very pronounced color and are considered as the mother substances of most of the dyes. (Willstätter and Piccard, *Ber.* **41**, 1465 (1908).)

[6] *Ber.*, **42**, 4339 (1909).