[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO]

THE CONDENSATION OF AMINOANTIPYRINE WITH AROMATIC AMINES IN THE PRESENCE OF OXIDIZING AGENTS*†‡

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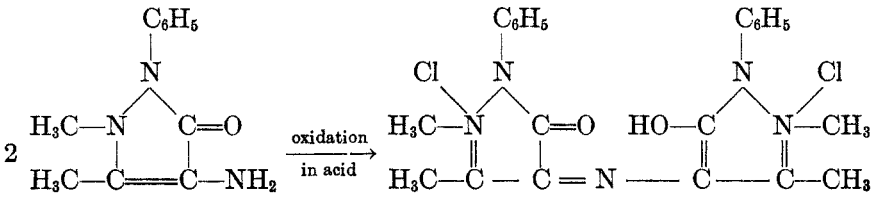
Aminoantipyrine can be oxidized to antipyrine red.[1] During the reaction one mole of ammonia is eliminated from two moles of aminoantipyrine.



This reaction suggested to the writer the possibility of producing indamine-type dyes by oxidizing mixtures of aminoantipyrine and an aniline. With this idea in mind, the oxidation of aminoantipyrine was carried out in the presence of various aromatic amines. New dyes were formed ranging in color from orange-red, through blue, to green, depending on the amine used. Phenols also were found to give color reactions with aminoantipyrine, but the conditions under which the phenols react are entirely different from those under which the amines react. The research reported in this paper is confined to the reaction of aminoantipyrine with aromatic amines.

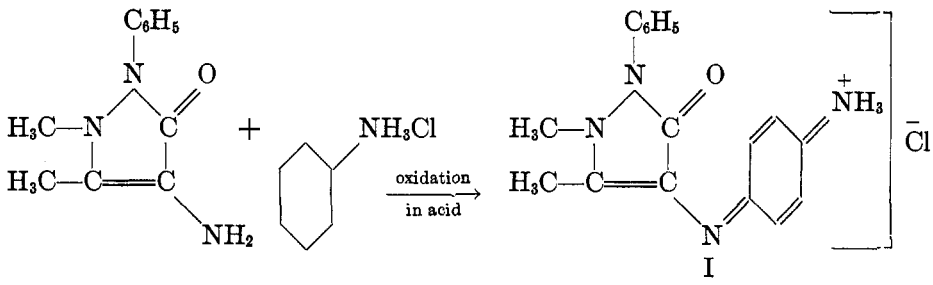
When aminoantipyrine, in solution with an equivalent of aniline hydrochloride, is oxidized with four equivalents of ferric chloride a blue-red dye is produced.

* The Dissertation submitted to the graduate faculty of The University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

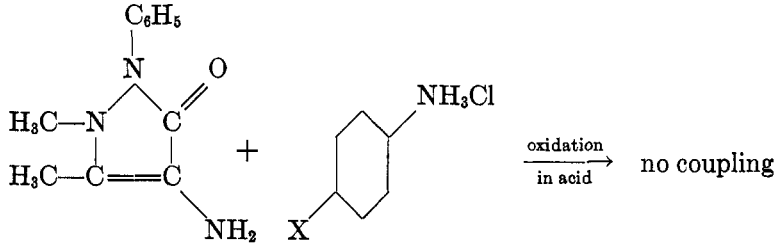
† It has been my great privilege to have worked on this research under the inspiring guidance of Professor Julius Stieglitz. I wish to express my appreciation to Dr. R. W. Johnson for his interest and criticisms in this work, and also I wish to thank Professor M. S. Kharasch for his suggestions during the last stages of this research. During the work I have had the advantage of the help and suggestions of my friend Dr. John Cryer.

‡ I wish to express my gratitude for a Julius Stieglitz Fellowship, the money for which was donated by the Chemical Foundation.

[1] MICHAELIS, *Ann.*, **352**, 157 (1907).

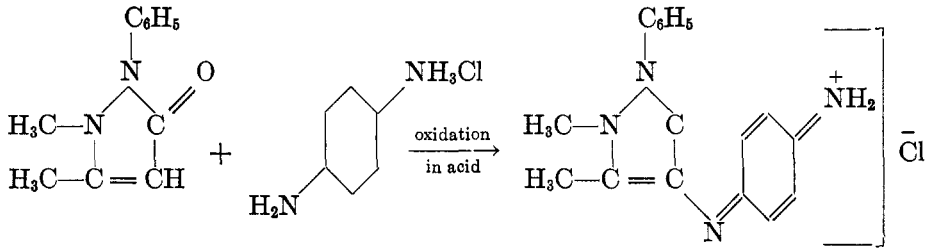


If *p*-toluidine, *p*-phenylenediamine or sulfanilic acid is used in place of aniline the reaction does not take place.



This evidence indicates that the dye formation involves the para hydrogen rather than the aromatic amine hydrogen. This view is supported by the fact that dimethylaniline with aminoantipyrine gives the color reaction, whereas *p*-bromodimethylaniline with aminoantipyrine does not.

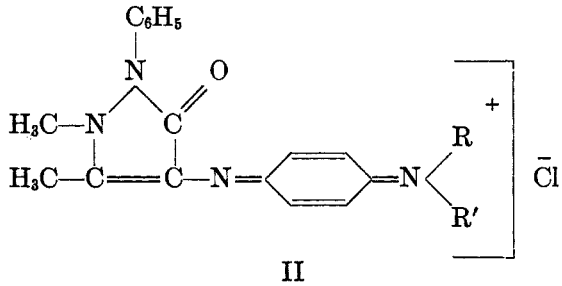
One might expect the oxidation of a mixture of antipyrine with *p*-phenylenediamine to produce the same colored compound as aminoantipyrine and aniline.



The indicated reaction does not take place. Dimethylaniline and antipyrine fail to give a distinguishing color reaction. If dimethylaminoantipyrine (pyramidon) is used in place of aminoantipyrine with a para-unsubstituted amine hydrochloride, only the blue color characteristic of oxidized pyramidon is produced. These facts indicate that the primary amino group in aminoantipyrine is involved in the color production.

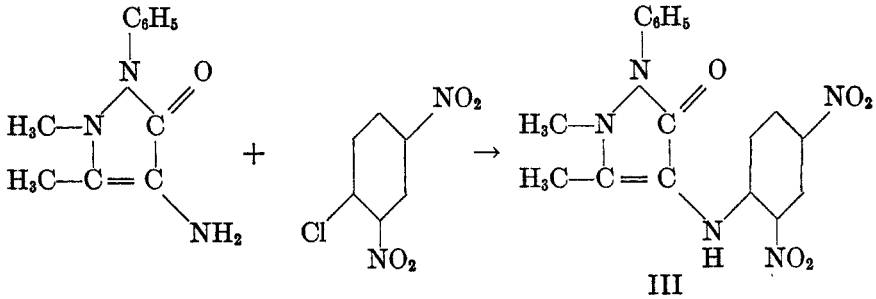
The results of these various reactions led to the belief that the dyes

might have the structure exemplified by the following formula (II), in which R and R′ may be aryl or alkyl groups or hydrogen.



II

The formation of the nitrogen-to-carbon linkage was established by the reaction between aminoantipyrine and 2,4-dinitrochlorobenzene. Analysis of the product formed in the reaction§ corresponded to the composition $C_{17}H_{15}N_5O_5$ (formula III).



III

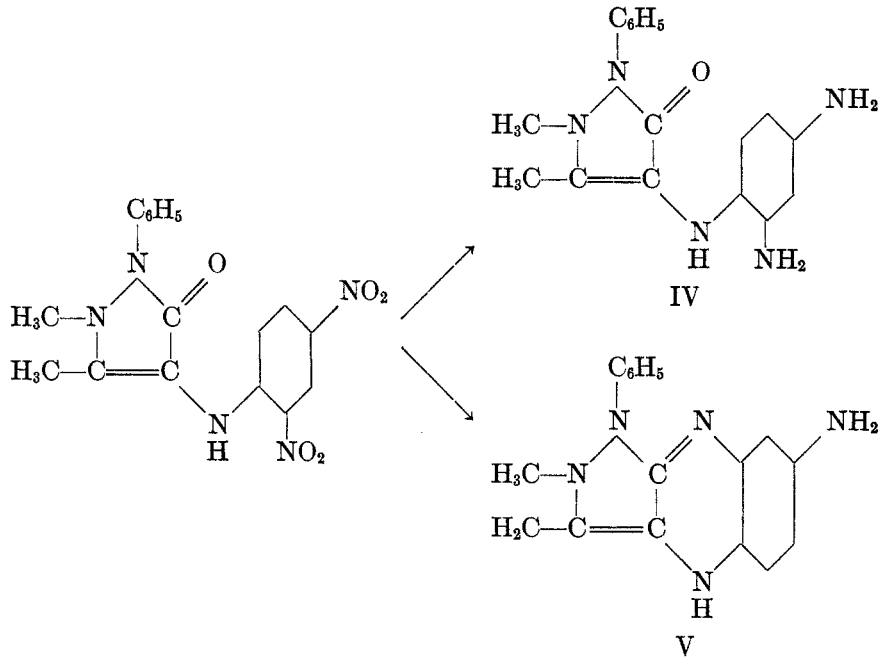
The reduction of the nitro groups in 2,4-dinitrophenylaminoantipyrine (formula III) would be expected to yield either or both of two possible compounds.

The analysis of the compound isolated corresponded to the composition $C_{17}H_{19}N_5O$ (formula IV), and not to $C_{17}H_{17}N_5$ (formula V).

It may be argued that cyclization occurred, as represented by formula V, but that the compound crystallized with a molecule of water of crystallization. The compound recrystallized from benzene was heated for two hours at 100° in a vacuum over phosphorus pentoxide without loss of weight. No indication of evolution of water was observed in the process of determining the melting point, even though the latter was 164.9–167.9°, well above the boiling point of water.

The results obtained from the analysis of the hydrochloride of the compound, recrystallized from alcohol and ether, did not indicate ring forma-

§ All the analyses shown in this paper were made by a professional analyst, Mr. Kurt Eder.



IV

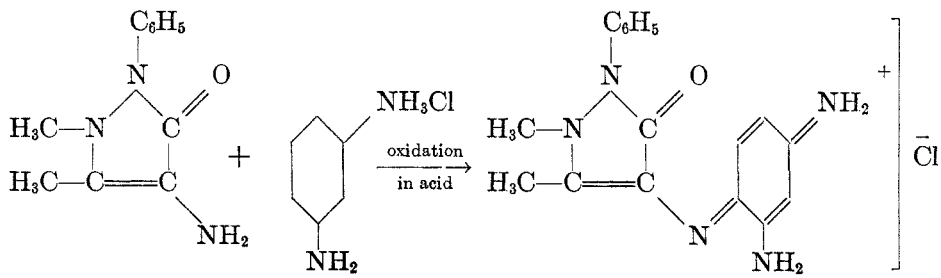
V

tion. Furthermore, no evolution of water was observed during the melting of the hydrochloride at 259.5–260.5°.

Finally, the dye produced by the oxidation of 2,4-diaminophenylaminoantipyrine hydrochloride was identical with the dye produced from the oxidation of a mixture of aminoantipyrine with *m*-phenylenediamine. The results obtained from the analysis of the dye did not indicate ring closure.

On the basis of evidence derived from the analysis of 2,4-diaminophenylaminoantipyrine, the leuco base of the dye, and its derivatives, formula IV should be assigned to the compound.

Oxidation of a mixture of *m*-phenylenediamine and aminoantipyrine forms a dye which dyes silk and wool directly a fast shade of burnt sienna.



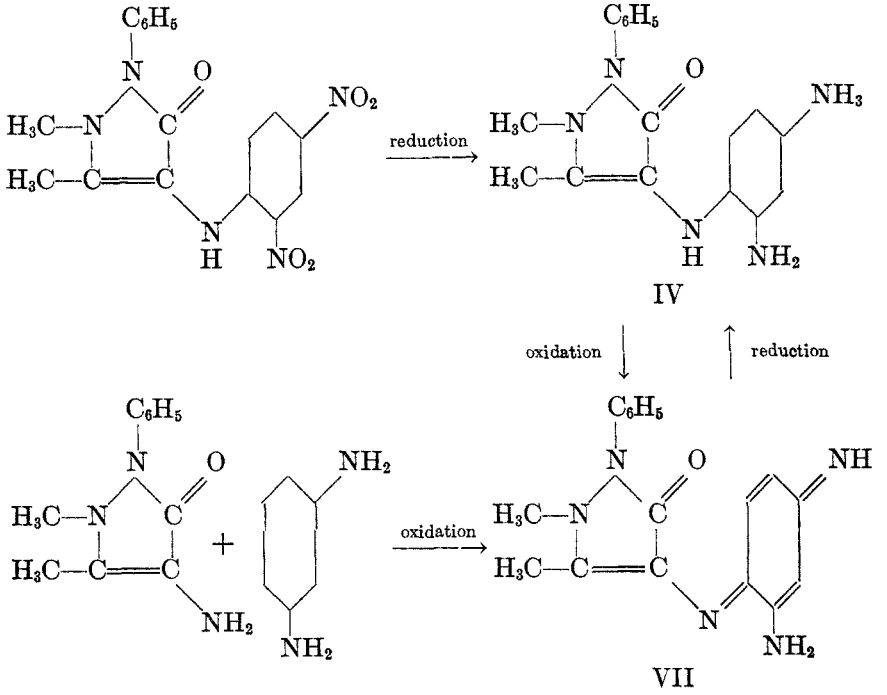
VI

The hydrochloride of the dye crystallizes from water, without the necessity of adding salt, and is easily purified in this manner. The analysis of the hydrochloride of the dye corresponds to that of the substance represented by formula VI. As the dye burns with difficulty a nitrogen analysis was unobtainable.

The absorption spectrum of the dye gives a peak of maximum absorption at 4800 ± 25 Å. (Figure 1.) The dye made from the reduction product of 2,4-dinitrophenylaminoantipyrine matches the color of the dye described above and gives an absorption curve that is identical with that obtained from the product of the reaction of aminoantipyrine with *m*-phenylenediamine. Thus it may be concluded that the two substances are identical.

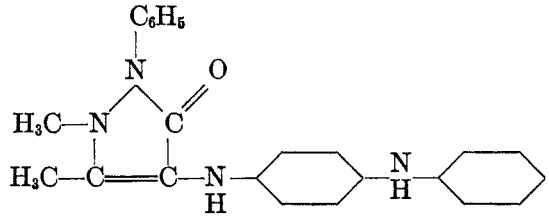
The analysis of the hydrochloride of the leuco compound prepared from the dye derived from *m*-phenylenediamine and aminoantipyrine gave results from which the formula $C_{17}H_{20}ClN_5O$ can be calculated.

The melting point of the compound was 258.6–259.1°. A mixture of the two leuco compounds prepared by different methods melted at 260.0–260.5°, which is the same temperature, or slightly higher, than the melting points of the substances taken separately. Thus it appears that the leuco compounds are identical.



Since the leuco compound made by reducing 2,4-dinitrophenylaminoantipyrine establishes the nitrogen-to-carbon bond, it follows that during the oxidation of aminoantipyrine and *m*-phenylenediamine a nitrogen-to-carbon bond is formed.

The predicted composition of the compound formed by the oxidation of a mixture of aminoantipyrine and diphenylamine would be $C_{23}H_{20}N_4O$. The dye was never obtained in a form sufficiently pure for analytical purposes but the leuco compound produced from the impure dye was easily purified. Results obtained from the analyses indicate the composition $C_{23}H_{22}N_4O$ (formula VIII).



VIII

Failure of di-*p*-tolylamine to produce the color reaction, when oxidized, in the presence of aminoantipyrine, is contributory evidence in support of the conclusion that the condensation produces a compound having a nitrogen-to-carbon bond, rather than a nitrogen-to-nitrogen bond.

The dye as represented in formula VI is a para quinoid. It is possible that it should be written as an ortho quinoid or as an equilibrium between the two types. This detail of the structure is still open to question, but by analogy no doubt is left as to the structure of the dyes formed from the aromatic monamines which may be represented, in general, by formula II.

The conditions necessary for the production of the antipyryl dyes, herein described, are strikingly similar to the conditions necessary for the production of the indamines. The indamines were discovered in 1877 by Nietzki,[2] who established their constitution[3] in 1883. He discovered that in order to obtain indamine dyes the amines should fulfill the following conditions:[4] The *p*-diamine must contain one free amino group, while the other may be primary, secondary, or tertiary; the monamine may be primary, secondary, or tertiary, but the position para to the amino group must be free. These conditions are exactly the same as those necessary

[2] NIETZKI, *Ber.*, **10**, 1157 (1877).

[3] NIETZKI, *ibid.*, **16**, 464 (1883).

[4] NIETZKI, "Chemie der Organischen Farbstoffe," Verlag von Julius Springer, Berlin, 5th Ed., **1906**, pp. 198–9.

for the production of the antipyryl dyes. The primary amine group in aminoantipyrine functions like the free amine group in the *p*-diamines.

The analogy of aminoantipyrine to the *p*-diamines extends beyond the reactions of the former with aromatic amines. It was mentioned in the first paragraph of this paper that phenols also give color reactions with aminoantipyrine. While the chemistry of this reaction has not been thoroughly investigated, sufficient work has been done to convince the writer that the reactions of aminoantipyrine with phenols are analogous to the reactions of the *p*-diamines with phenols in which indophenols[5] are formed.

Finally, it may be mentioned that nitrosoantipyrine reacts with diphenylamine to produce a dye the solutions of which appear to be identical in color with solutions of the dye produced from the reaction of aminoantipyrine and diphenylamine. If the dyes are identical, then the latter reaction is analogous to the reaction of *p*-nitrosoamines with secondary or tertiary, para-free, amines. Sufficient work has not been done on the reaction to make definite claims but the work done up to date indicates that the analogy is complete.

EXPERIMENTAL

Preparation of nitrosoantipyrine.—Nitrosoantipyrine was prepared by the method described by Rodinow[6] with but slight modification. Antipyrine (188 g.) was dissolved in 1500 cc. of water. After the addition of 100 cc. of concentrated hydrochloric acid the solution was cooled to 5–0°. With good mechanical stirring over a period of one hour, 75 g. of sodium nitrite dissolved in 300 cc. of water was introduced below the surface of the liquid. The resulting green solution was kept between 0° and 5° throughout the reaction. The stirring was continued for fifteen minutes after the last of the nitrite had been added. The copious green precipitate of nitrosoantipyrine which formed during the reaction was separated by filtration and washed with two liters of cold distilled water.

Preparation of aminoantipyrine.—The following modification of the procedure described by Rodinow[6] was found to give, not only better yields, but also the free base directly instead of the hydrochloride of aminoantipyrine. The wet nitrosoantipyrine, produced as described above, was transferred to a two-liter filter flask, fitted with a mercury seal for stirring. (The mercury in the seal was protected from the action of hydrogen sulfide by a layer of glycerin.) Distilled water (1500 cc.) containing 5 cc. of concentrated ammonium hydroxide was added, and the resulting suspension was stirred. Hydrogen sulfide was then passed into the reaction mixture until the green color changed to pale yellow (from one and a half to two hours). When the reduction was complete the mixture was heated on a steam bath for fifteen minutes, during which time the stirring and the passage of a slow stream of hydrogen sulfide were continued. The heating was for the purpose of coagulating the colloidally suspended sulfur. The hot solution was quickly filtered into a two-liter

[5] KOCHLIN, *Bull. Soc. ind. de Mulhouse*, **1882**, 532; O. WITT, *J. Soc. Chem. Ind.*, **1882**, 225.

[6] RODINOW, *Bull. soc. chim.*, **39**, 321 (1926).

filter flask. A small amount of sulfur passed through the filter, but this was removed in the subsequent filtration. The sulfur on the filter was washed with two 25-cc. portions of water containing hydrogen sulfide. These washings and 5 cc. of concentrated ammonium hydroxide were combined with the filtrate. The resulting solution was evaporated on a steam bath in a slow stream of hydrogen sulfide under reduced pressure. The vacuum was produced by means of a water pump. When the volume was reduced to 600–700 cc., the vacuum was broken with hydrogen sulfide and the liquid was filtered into a one-liter filter flask. The evaporation was continued under reduced pressure to dryness. The last trace of water was removed by the use of an oil pump pulling through a calcium chloride tower. This treatment yielded a viscous syrup which, after about thirty-six hours, crystallized to a pale yellow compact mass which weighed 183 g., and melted at 100.0–103.1°. This was a 90% yield based on antipyrine.

The product was purified by crystallization from an equal weight of boiling benzene; m.p. 109.0–109.5°.

Preparation of Antipyryl Red B-3.—Aminoantipyrine (4.1 g.) and *m*-phenylenediamine dihydrochloride (3.6 g.) were dissolved in 100 cc. of water. The resulting solution was cooled by the addition of 200 g. of crushed ice. To this mixture 22 g. of ferric chloride hexahydrate in 40 cc. of water was added at once, and then 300 cc. of saturated sodium chloride solution. After ten minutes the precipitated dye was brought on a filter and washed with saturated sodium chloride solution until the wash water no longer gave a test for iron with ammonium thiocyanate.* When all the iron salts had been removed by washing, as much of the wash water as possible was pressed from the dye on a suction filter. The cake formed on the filter was transferred to 500 cc. of water at 80° and stirred at that temperature for five minutes. The solution was then filtered hot, and as the filtrate cooled, red needles were deposited. The product was purified by crystallization from water, and dried in a vacuum desiccator over phosphorus pentoxide. As the drying proceeded, the dye became darker in color until it was a dark garnet red. The garnet red crystals when rubbed on a watch glass with a glass rod showed a bright green reflex.

The dye is soluble in water, alcohol, acetone, and dioxane, and insoluble in hydrocarbon solvents, chloroform, and ether.

Anal. Calc'd for $C_{17}H_{18}ClN_5O$: C, 59.38; H, 5.28; Cl, 10.33.
Found: C, 59.29; H, 5.30; Cl, 10.29.

Since these analyses are for the compound produced by the above procedure, that method of necessity was described. However, the procedure was subsequently improved, to increase the yield, in the following manner. Aminoantipyrine (4.1 g.) and *m*-phenylenediamine (3.6 g.) were dissolved in 60 cc. of water. When solution was complete, 2.1 g. of anhydrous sodium carbonate was added. The solution was filtered, the filtrate was diluted with water to 100 cc., and 100 g. of crushed ice was added. To the reaction mixture a filtered solution of 22 g. of ferric chloride hexahydrate in 15 cc. of water was added at once. From this point on the procedure was the same as that described above.

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* The iron test was carried out in the following manner. To 2 to 3 cc. of wash water was added one drop of hydrogen peroxide, followed by the addition of 0.5 cc. of ten per cent ammonium thiocyanate solution. The solution was shaken with about 2 cc. of ether. Since the mineral acid salts of the dye are insoluble in ether any red color appearing in the ether layer is due to the presence of iron. This test can be used regardless of the intensity of the color of the dye solution.

Reduction of Antipyryl Red B-3 to the leuco compound.—To four grams of Antipyryl Red B-3, suspended in 100 cc. of water was added 4 g. of sodium hydrosulfite in 40 cc. of water. The solution was shaken until all the red color was discharged. Hydrogen sulfide was passed into the solution, which was then filtered. After 5 cc. of 6*N* sodium hydroxide was introduced into the filtrate, silky white needles were deposited. When the deposition was complete, the crystalline precipitate was brought on a sintered glass filter, and washed with two 10 cc. portions of water saturated with hydrogen sulfide. The crystals were quickly transferred to a vacuum desiccator filled with nitrogen over phosphorus pentoxide. The desiccator was exhausted, and the product was allowed to dry for twelve hours. All operations with the leuco compound must be performed quickly, and contact with air must be avoided as much as possible to prevent undue oxidation.

The dry leuco compound was refluxed for fifteen minutes in 200 cc. of benzene. The hot benzene solution was filtered to remove a reddish sludge. On cooling, the filtrate deposited silky white needles which soon turned pink on exposure to the air.

Soluble in benzene, ether and chloroform; slightly soluble in water; m.p. 264.9–267.9°.

Anal. Calc'd for $C_{17}H_{19}N_5O$: C, 66.02; H, 6.15; N, 22.65; O, 5.18.
Found: C, 66.52; H, 6.08; N, 22.23; O (by difference), 5.17.

Preparation of the leuco hydrochloride of Antipyryl Red B-3.—One-half gram of leuco Antipyryl Red B-3 was treated with 1 cc. of concentrated hydrochloric acid. After the addition of 15 cc. of alcohol, the mixture was warmed to complete the solution of the hydrochloride. The solution was then filtered through a sintered glass filter. When the filtrate was sufficiently cool 15 cc. of ether was added. The solution was allowed to cool for one hour at about 5°, during which time a white crystalline precipitate formed. The crystals were brought on a filter and washed with 1:1 alcohol-ether. The washed crystals were dissolved in 50 cc. of boiling alcohol. Dissolution was slow and not all of the material dissolved. The solution was then filtered, and 50 cc. of ether was added to the filtrate, which was allowed to cool at 5°. The crystals formed were separated by filtration and washed as described above. This process was repeated three more times, and the crystals were finally dried in a vacuum desiccator over phosphorus pentoxide.

Soluble in hot water and hot alcohol; insoluble in ether, benzene and chloroform; m.p. 258.6–259.1°.

Anal. Calc'd for $C_{17}H_{18}ClN_5O$: Cl, 10.26. Found: Cl, 10.29.

Preparation of 2,4-dinitrophenylaminoantipyrine.—Aminoantipyrine and 2,4-dinitrochlorobenzene, when heated to 110°, were found to react directly to form 2,4-dinitrophenylaminoantipyrine. It was further found that, in the presence of sodium carbonate, the reaction occurred at a lower temperature and gave a product more readily soluble in alcohol.

Two parts, by weight, of aminoantipyrine were ground with two parts of 2,4-dinitrochlorobenzene and one part of anhydrous sodium carbonate. This mixture was warmed on a steam bath until the melt solidified to an orange-red solid. This was refluxed with one hundred parts of alcohol, until all the organic material dissolved. The alcoholic solution was filtered, and the residue was extracted with twenty-five parts of boiling alcohol. The extract and filtrate were then combined and evaporated to one-tenth the original volume. This mixture was cooled and the orange crystalline product was brought on a filter and washed with cold alcohol.

Yield, about 70% of pure material; m.p. 213.1–213.9°.

Anal. Calc'd for $C_{17}H_{15}N_5O_5$: C, 55.28; H, 4.09; N, 18.96; O, 21.67.
Found: C, 55.27; H, 3.91; N, 19.04; O (by difference), 21.78.

Slowly soluble in hot alcohol, soluble in acetic acid and hydrochloric acid. Insoluble in ether and water. Best crystallized from hot chlorobenzene. Alkaline solutions added to alcoholic solutions of 2,4-dinitrophenylaminoantipyrine turn them deep red.

Reduction of nitro groups in 2,4-dinitrophenylaminoantipyrine.—Iron, tin, or zinc will reduce both nitro groups of 2,4-dinitrophenylaminoantipyrine in acid solution. Two and a half grams of the nitro compound was dissolved in 25 cc. of concentrated hydrochloric acid. Over a period of three hours, 7.5 g. of granulated tin were added. It was necessary for stirring to be efficient to keep the heavy yellow precipitate that formed at first from caking. After the first hour the reaction mixture was heated to boiling, from time to time, to keep the reaction going briskly. When the reduction was complete, as indicated by the disappearance of the yellow color, the solution was filtered from the excess tin and the filtrate poured into 75 cc. of 6*N* sodium hydroxide solution, which was then extracted with ten 20-cc. portions of chloroform. The extract was boiled to assure solution of all organic material. During the boiling the solution was protected by an atmosphere of carbon dioxide, which served to prevent exposure of the leuco compound to atmospheric oxygen. The extract was filtered, and the filtrate was evaporated to dryness in a stream of carbon dioxide. To the syrupy residue, 2 cc. of concentrated hydrochloric acid was added, and then 50 cc. of alcohol. This mixture was boiled in a stream of carbon dioxide, and when solution was complete the solution was filtered. To the filtrate 50 cc. of ether was added, and the solution was allowed to cool for twelve hours at about 5°. The white crystalline solid which formed during the cooling was then separated by filtration, and the residue was washed with 1:1 alcohol-ether. The 2,4-diaminophenylaminoantipyrine hydrochloride was purified by crystallization from a minimum amount of air-free water. The almost-white crystals were dried in a vacuum desiccator over phosphorus pentoxide; m.p. 259.5–260.5°. The melting point of the mixture of these crystals and the crystals of the previously described leuco hydrochloride is 260.0–260.5°.

Anal. Calc'd for $C_{17}H_{18}ClN_5O$: C, 59.00; H, 5.84; N, 20.25; Cl, 10.27; O, 4.64.
Found: C, 59.63; H, 5.67; N, 19.30; Cl, 10.79; O (by difference), 4.61.

The compound is the leuco hydrochloride of Antipyryl Red B-3.

Oxidation of leuco hydrochloride made from 2,4-dinitrophenylaminoantipyrine.—To 10 cc. of water, 0.20 g. of the leuco hydrochloride made from the reduction of 2,4-dinitrophenylaminoantipyrine was added. The mixture was boiled to complete dissolution, then cooled to about 50°, and 0.50 g. of ferric chloride hexahydrate in 1 cc. of water was added. Next, 20 cc. of saturated sodium chloride solution was added. The precipitated red dye was separated by filtration and washed with saturated sodium chloride solution until the test for iron† with ammonium thiocyanate was negative. The dye was pressed on the filter and washed with 3 cc. of water, after which it was dissolved in 3 cc. of water at 65°. The hot solution was filtered through a sintered glass filter, and the filtrate allowed to stand at about 5° for one-half hour, after which the dye was brought on a filter and washed with 3 cc. of cold water. The product was dried in a vacuum desiccator over phosphorus pentoxide.

The absorption spectrum of Antipyryl Red B-3 made by two different methods.‡—Samples of Antipyryl Red B-3 prepared by the two methods described above were

† See previous footnote.

‡ The absorption spectra measurements were made by Dr. Albert E. Sidwell, Jr., in this laboratory.

used to determine absorption spectra. Weighed portions were dissolved in Sörensen's phosphate buffer of pH 6.73,[7] and were examined spectrophotometrically.[8] The solutions were compared with a portion of the diluent buffer solution. Quartz absorption cells two centimeters in length were employed. The results of the determination of the specific absorption, in the region 4000 Å. to 7000 Å., of the two samples are shown graphically in the accompanying figure.

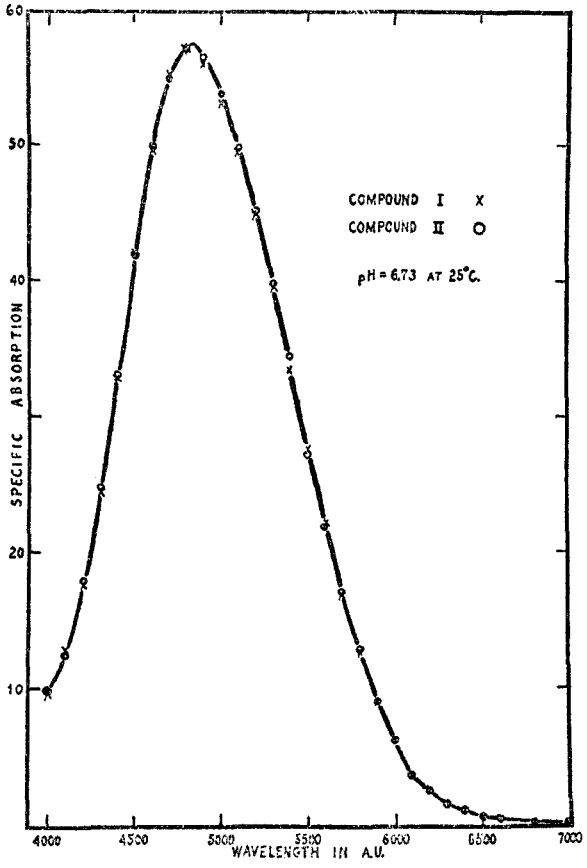

FIGURE.—ABSORPTION SPECTRA OF TWO SAMPLES OF ANTIPYRYL RED B-3

Preparation of Antipyryl Blue A-93.—Two solutions were prepared as follows. Solution I contained 2.0 g. of potassium dichromate, 2.0 cc. of concentrated sulfuric acid, and 25 cc. of water. Solution II contained 2.0 g. of aminoantipyrine, 1.7 g. of diphenylamine, and 25 cc. of glacial acetic acid. Solution II was cooled in an ice bath, and while it was being stirred Solution I was added. After the reaction

[7] CLARK, "The Determination of Hydrogen Ions," Williams & Wilkins Co., Baltimore, 3rd Ed., **1928**, p. 210, Table 41.

[8] HOGNESS, ZSCHEILE, AND SIDWELL, *J. Phys. Chem.*, **41**, 379 (1937).

mixture was poured into 500 cc. of water the resulting solution was filtered. The filtrate, cooled in an ice-salt bath, was well stirred while 200 g. of sodium chloride was added. After fifteen minutes, the precipitated blue dye was separated by filtration and washed with saturated sodium chloride solution. As much of the sodium chloride solution as possible was pressed out, and the dye was dried in a vacuum desiccator over phosphorus pentoxide.

The dried material is difficultly soluble in water; it dissolves in alcohol, acetic acid, or formic acid to form beautiful pure-blue solutions. It is also soluble in concentrated sulfuric acid, forming an intense cerise solution.

Reduction of Antipyryl Blue A-93.—One-half gram of Antipyryl Blue A-93 was dissolved in 50 cc. of acetone. The solution was filtered and to the filtrate five per cent. sodium carbonate solution was added until the color changed from blue to bright red. A freshly prepared ten per cent. solution of sodium hydrosulfite was added drop by drop to this solution until the red color was discharged. The colorless liquid was poured into 1500 cc. of water containing a trace of ammonium sulfide. The flocculent precipitate was brought on a filter and washed with water, in which was dissolved a few drops of ammonium sulfide solution. The residue on the filter was dissolved in 50 cc. of boiling acetone, and one liter of water containing a trace of ammonium sulfide was added to precipitate the leuco base. This procedure was repeated eight times. Finally, the product was dissolved in a minimum amount of boiling acetone, and the solution allowed to cool. The white crystals, which were fairly stable towards air oxidation, were separated from the solution by filtration; m.p. 220.3–221.8°.

Difficultly soluble in hot acetone, alcohol, or benzene; insoluble in water.

Anal. Calc'd for $C_{23}H_{22}N_4O$: C, 74.55; H, 5.99; N, 15.14; O, 4.32.
Found: C, 74.61; H, 5.84; N, 15.17; O (by difference), 4.38.

SUMMARY

(1) A new color reaction between 4-aminoantipyrine and para-unsubstituted aromatic amines has been described.

(2) Several of the dyes obtained by the above reaction have been described.

(3) The structures of these dyes have been determined.

(4) The limiting conditions for the reaction have been discussed.

(5) An analogy between 4-aminoantipyrine and the *p*-phenylenediamines has been drawn, based on the color reaction.

(6) The analogy has been made more complete by mention of the following facts:

(*a*) phenols react with 4-aminoantipyrine to produce dyes similar to the indophenols.

(*b*) nitrosoantipyrine reacts with diphenylamine in a manner similar to para nitrosoamines.

(7) The following new compounds have been prepared:§

§ Ap- is used to represent the antipyryl radical.

(*a*)	Ap—N=$C_6H_3(NH_2)$=NH_2Cl (2, 4)	Antipyryl Red B-3 (Formula VI)
(*b*)	Ap—N(H)—$C_6H_3(NH_2)$—NH_3Cl (2, 4)	2,4-Diaminophenylaminoantipyrine hydrochloride (Hydrochloride of Formula IV)
(*c*)	Ap—N(H)—$C_6H_3(NH_2)_2$ (2,4)	2,4-Diaminophenylaminoantipyrine (Formula IV)
(*d*)	Ap—N(H)—$C_6H_3(NO_2)_2$ (2,4)	2,4-Dinitrophenylaminoantipyrine (Formula III)
(*e*)	Ap—N=C_6H_4=N—$C_6H_5\cdot HCl$	Antipyryl Blue A-93
(*f*)	Ap—N(H)—C_6H_4—N(H)—C_6H_5	*N*, *N'*-Antipyryl phenyl *p*-phenylenediamine (Formula VIII)