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DIMETHYLDIPHENYL-PARA-PHENYLENEDIAMINE AND THE COLOR OF MONO SALTS AND DI SALTS OF HOLOQUINONIC COMPOUNDS

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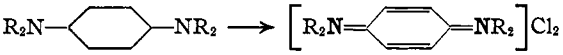
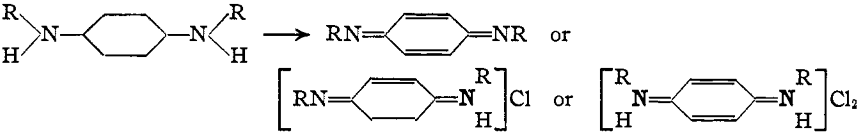
If we oxidize any tetrasubstituted phenylenediamine or benzidine to the corresponding holoquinonic salt, we shall always obtain a salt with two molecules of acid, a "di salt."[1]



The above formula shows clearly that it is not possible to obtain either an imino base or a salt with only one molecule of a univalent acid ("mono salt"). Symmetrically disubstituted phenylenediamines or benzidines, however, may produce on oxidation the free imino base, the mono salt or the di salt.



The salts always have a deeper[2] color than the imino base. While working in this field I found the following interesting and very general rule: quinonedi-imines and diphenoquinonedi-imines (that is, the holoquinonic benzidine derivatives) give mono salts that have a deeper color than the corresponding di salts.

For this reason diphenylbenzidine gives a blue holoquinonic salt and dimethyldiphenylbenzidine, newly prepared by Wieland[3] does not give, as that author expected it to do, a holoquinonic salt of deeper color (for instance, greenish-blue), but it gives a holoquinonic salt of a less deep color, violet-red. This observation induced Wieland to serious doubts of the old law that substitution deepens the color. We were able to show[4] that Wieland had compared the blue color of the mono salt derived from diphenylbenzidine with the color of the salt derived from dimethyldiphenylbenzidine which, of course, must be a di salt. We were able to show that in the case of diphenylbenzidine the holoquinonic mono salt is changed by the addition

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[1] We use the coördination formula; see Ref. 4 in the preceding paper.

[2] In the succession of colors yellow, orange, red, violet, blue, green, each is classed as "deeper" than the preceding one.

[3] Wieland, *Ber.*, **52**, 886 (1919).

[4] Piccard, *Helvetica Chim. Acta*, **7**, 790 (1924).

of fuming sulfuric acid,[5] its color becomes less deep; it is only violet and there is no doubt that if we could have solutions of the pure di salt, they would be only violet-red.

If our explanation of Wieland's observations is correct, we must confront a similar phenomenon when we compare the holoquinonic salts derived from diphenyl-*p*-phenylenediamine with those derived from dimethyldiphenyl-*p*-phenylenediamine. Since this base has not yet been described, we were obliged to synthesize it. The difficulties that arose showed us why such a relatively simple compound could not be found in the literature.

If the solution of this new base in 95% acetic acid is oxidized, the blue color of the meriquinonic salt[6] first appears and then the color of the holoquinonic salt. It is red, whereas the non-methylated base gives under similar conditions a deeper color, violet-red. By these reactions we have shown that in the phenylenediamine series exactly the same thing happens which had happened in the benzidine series; in acetic acid solution it is the non-methylated holoquinonic salt that has the deeper color, because the non-methylated derivative gives a mono salt and the methylated one must give a di salt.

First Synthesis,[7] $C_6H_5N(CH_3)\boxed{H + I}C_6H_4\boxed{I + H}(CH_3)NC_6H_5$.—A mixture of 16.5 g. of *p*-di-iodobenzene[8] and 32 g. of monomethylaniline was heated 25 hours at 200° to 230° with 85 g. of potassium carbonate and 12 cc. of nitrobenzene in the presence of a few milligrams of catalytic copper.[9] The product of the condensation was isolated as usual. Steam was passed through the reaction mixture which took away any unchanged methylaniline and the nitrobenzene. Then benzene was added and the organic products were separated from the inorganic compounds and the copper powder.

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[5] Kehrmann indicates that azobenzene produces a di salt when dissolved in fuming sulfuric acid. It is certainly correct that fuming sulfuric acid produces a compound which has the color of the di salt, but we doubt that it produces what is really a di salt. The coördinatively only trisubstituted ammonia nitrogen atom is not likely to add hydrogen ions in fuming sulfuric acid if it is not basic enough to do so in concd. sulfuric acid, because in fuming sulfuric acid hydrogen ions are rather few. It seems more likely to pick sulfur trioxide molecules out of the solution. We relate in this connection our observation that many bases which dissolved under salt formation (that is, addition of hydrogen ions) in dil. acetic acid are soluble without salt formation in acetic acid if there is less than 5% of water in it. The solution in glacial acetic acid has on that account the color of the benzene solution of the free base. A small addition of water produces instantaneously the color of the salt because it produces hydrogen ions. It shows that the acetate is not formed by the absorption of acetic acid of which there is plenty in glacial acetic acid, but by absorption of hydrogen ions. It shows also the superiority of the coördination formula for the explanation of salt formation.

[6] See the following paper.

[7] This method for the introduction of phenyl groups into amino groups was invented by F. Ullmann [*Ber.*, **36**, 2838 (1903)]. For further details see Piccard and de Montmollin, *Helvetica Chim. Acta*, **6**, 1016 (1923).

[8] *p*-Dibromobenzene does not react sufficiently.

[9] Piccard, *Helvetica Chim. Acta*, **5**, 147 (1922).

In other cases the evaporation of the benzene solution yielded the desired base in sufficiently pure form to allow further purification by ordinary recrystallization. In this case, however, we obtained only gluey, black mixtures, which gave not even the color reactions that we expected from our new base. In order to extract our dimethyldiphenylphenylenediamine we added to the benzene solution an equal amount of concd. hydrochloric acid. This operation converted all of the bases into hydrochlorides, leaving in the benzene solution only acid or neutral compounds which did not interest us. Both layers were separated and the hydrochloric acid solution was treated with two and one-half times its volume of water. This in turn precipitated the weak bases such as dimethyldiphenylphenylenediamine. These weak bases were again extracted with benzene and the solution was dried and evaporated in a vacuum. A brown, tarry mass was obtained which, however, soon produced crystals of the desired base. These crystals were isolated by pressing the mass on porcelain and then washing them carefully with a few drops of benzene and again with a small amount of alcohol. Dimethyldiphenyl-*p*-phenylenediamine, recrystallized from alcohol, forms colorless prisms which are often 15 to 20 mm. long. It is very soluble in benzene and in alcohol, but only slightly soluble in glacial acetic acid; m. p., 147–151° (corr.).

Anal. Subs., 0.1764: 15.4 cc. of N_2, (17°, 719 mm. (corr., 712)). Calcd. for $C_{20}H_{20}N_2$: N, 9.72. Found: 9.63.

Second Synthesis, $C_6H_5N(CH_3)\boxed{H + HO}C_6H_4\boxed{OH + H}(CH_3)NC_6H_5$.—Calm[10] had prepared diphenyl-*p*-phenylenediamine by heating hydroquinone with aniline in a sealed tube in the presence of calcium chloride and zinc chloride. For the synthesis of our base we replaced the aniline by monomethylaniline. The method gave very poor results and we obtained a base that by oxidation gave a holoquinonic salt, which changed color on the addition of concd. sulfuric acid. We have seen above that the holoquinonic salt derived from dimethyldiphenyl-*p*-phenylenediamine has two quaternary nitrogen atoms and must, therefore, give only one salt, a di salt. For this reason it cannot change color on the addition of a stronger acid. The observed change of color shows that during the condensation some of the methyl groups have migrated into the nucleus. By running the condensation very carefully we could, however, obtain enough dimethyldiphenyl-*p*-phenylenediamine to identify the base with that obtained by the first method. The color of the holoquinonic salt, as expected, does not change on addition of concd. sulfuric acid.

Third Synthesis, $C_6H_5\boxed{I + H}N(CH_3)C_6H_4N(CH_3)\boxed{H + I}C_6H_5$.—This method, starts with a compound that is rather difficult to make and the condensation does not give encouraging results. For these reasons we stopped working on this line.

Fourth Synthesis, $C_6H_5NHC_6H_4NHC_6H_5 + (CH_3)_2SO_4$.—Five-tenths g. of diphenyl-*p*-phenylenediamine was heated on the water-bath during ten minutes with 4 cc. of dimethyl sulfate. After treatment with sodium hydroxide the base was extracted with benzene and purified by conversion into the hydrochloride as described above. This synthesis is by far the best and if the necessary diphenyl-*p*-phenylenediamine is available it is also a very rapid way to make dimethyldiphenyl-*p*-phenylenediamine. The methylation in alkaline solution does not go so well, nor did the methylation by other methods give good results.

Dimethyldiphenylbenzidine

This compound had been prepared by Wieland but by only a single method, the oxidation of methyldiphenylamine. We made two new syntheses of it; first, diphenylbenzidine was methylated with dimethyl sulfate,

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[10] Calm, *Ber.*, **16**, 2803 (1883).

and second, p,p'-di-iododiphenyl was treated with monomethylaniline. In both cases, we obtained dimethyldiphenylbenzidine which we could identify with the preparation made by Wieland, for the sample of which we wish to thank Professor Wieland.

It gives me great pleasure to acknowledge the valuable help of Dr. R. Bretagne at the University of Lausanne.

Summary

We have described the preparation of dimethyldiphenyl-*p*-phenylenediamine, and its identity was proved by the fact that we obtained the same compound by three different methods. On oxidation it shows the same characteristics as the corresponding benzidine derivative, dimethyldiphenylbenzidine. We have also carried out two new syntheses of this dimethyldiphenylbenzidine.

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[CONTRIBUTION FROM THE PLAUT RESEARCH LABORATORY OF LEHN AND FINK, INCORPORATED]

FURTHER STUDIES ON THE INTRODUCTION OF ALKYL AND ARYL GROUPS INTO THE NUCLEUS OF POLYPHENOLS

BY EMIL KLARMANN

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The alkyl and aryl substituted derivatives of resorcinol, some of which possess remarkable antiseptic properties, may be obtained by different methods. Thus, benzylresorcinol is prepared either by the direct introduction of the benzyl group into the nucleus of resorcinol or by the reduction of the corresponding *m*-dihydroxybenzophenone. The first way was used by Liebmann[1] who showed that aliphatic alcohols and benzyl alcohols, when heated with resorcinol in the presence of zinc chloride, combine with resorcinol and form the corresponding substitution derivatives. Klarmann[2] effected a substitution of resorcinol by the condensation of benzyl chloride with resorcinol in the presence of aluminum chloride in nitrobenzene solution. It may be mentioned here that Boeseken[3] considers benzyl chloride as unsuitable for the Friedel-Crafts reaction, since it is declared to lead to resinified products. The reduction of the *m*-dihydroxybenzophenone was studied by Hirzel,[4] Dohme[5] and Klarmann.[2] The ketone was obtained by the first two authors by direct condensation of benzoic acid with resorcinol in the presence of zinc chloride, according to

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[1] Liebmann, *Ber.*, **14**, 1842 (1881); Ger. pat. 17,311 (1881).

[2] Klarmann, THIS JOURNAL, **48**, 791 (1926).

[3] Boeseken, *Rec. trav. chim.*, **23**, 98 (1904).

[4] Hirzel, Brit. pat. 222,136 (1925).

[5] Dohme, Brit. pat. 223,190 (1925).