

**THE METHYLATION OF  
PARA-AMINOPHENOL BY  
MEANS OF  
FORMALDEHYDE**

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The methylation of para-aminophenol by means of formaldehyde by Ernest Carl Wagner

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**ERNEST CARL WAGNER**

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#### ACKNOWLEDGMENT

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Much practical help and many useful suggestions were given by Dr. H. S. Lukens.

To these gentlemen the writer takes this opportunity to express his appreciation.

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1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes that proper record-keeping is essential for ensuring transparency and accountability in financial reporting.

2. The second part of the document outlines the various methods and techniques used to collect and analyze data. It highlights the need for consistent and reliable data collection processes to ensure the validity of the results.

3. The third part of the document describes the different types of data that are collected and analyzed. It includes information on both quantitative and qualitative data, as well as the various sources from which the data is gathered.

4. The fourth part of the document discusses the various statistical methods and techniques used to analyze the data. It covers topics such as hypothesis testing, regression analysis, and correlation analysis, among others.

5. The fifth part of the document discusses the various ways in which the results of the analysis can be presented and communicated. It includes information on the use of tables, graphs, and charts to effectively convey the findings.

6. The sixth part of the document discusses the various factors that can influence the results of the analysis. It includes information on the potential for bias and error, as well as the importance of controlling for these factors.

7. The seventh part of the document discusses the various ways in which the results of the analysis can be used to inform decision-making. It includes information on the use of the results to identify trends and patterns, as well as to develop strategies and policies.

8. The eighth part of the document discusses the various ways in which the results of the analysis can be used to improve the quality of the data collection process. It includes information on the use of the results to identify areas for improvement and to develop new methods and techniques.

9. The ninth part of the document discusses the various ways in which the results of the analysis can be used to improve the overall quality of the organization. It includes information on the use of the results to identify areas for improvement and to develop new strategies and policies.

10. The tenth part of the document discusses the various ways in which the results of the analysis can be used to improve the overall quality of the industry. It includes information on the use of the results to identify areas for improvement and to develop new standards and practices.

# The Methylation of *p*-Aminophenol by Means of Formaldehyde

*A Study of Certain Methods for the Conversion  
of the Condensation-products of Formaldehyde  
and *p*-Aminophenol into *N*-Methyl-*p*-aminophenol*

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This paper is divided as follows:

*I- The Condensations of Formaldehyde and  
Aromatic Amines*

- A. Condensations in Neutral or Alkaline Media
- B. Condensations in Acid Media
- C. Summary of Important Condensations and  
Secondary Reactions

*II- Methylation of Aromatic Amines by Means  
of Formaldehyde*

*III- Experimental Results on the Methylation of  
*p*-Aminophenol by Means of Formaldehyde*

*IV- Summary*

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## I. The Condensations of Formaldehyde and Aromatic Amines

In the condensations of formaldehyde with the amines, the fundamental change consists in the splitting out of the elements of water, with the result that a methylene-group is introduced. Typically the necessary hydrogen atoms are displaced from an amino-group, or from two imino-groups. It is characteristic of certain condensations, however, that only nuclear hydrogen atoms are involved. The course of the condensation depends upon (a) the nature of the medium in which condensation occurs, *i.e.*, whether neutral, alkaline, or acid, (b) the relative proportions of amine and aldehyde, (c) the presence of substances with which further reaction may occur, and (d) the influence of substituent groups present in the amine molecule.

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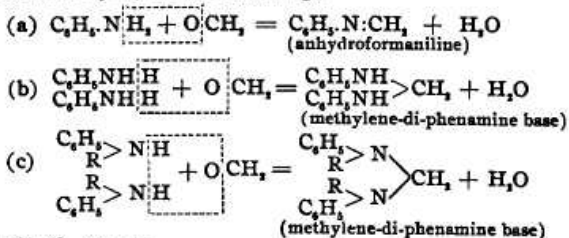
### METHYLATION OF PARA-AMINOPHENOL

With respect to these influences, it can be said introductorily that what may be termed the normal condensation occurs in neutral or alkaline solution, that which results in presence of acid being essentially different. The relative amounts of amine and aldehyde present determine whether one or two amine molecules will be involved in the condensation, and also, when an excess of amine-salt is present, whether or not further condensations of the primary product with uncondensed amine will occur.

The influence of substituent groups upon aldehyde condensations was observed by Eibner<sup>1</sup> who found that trichloraniline did not react with chloral, though less chlorinated anilines condensed. In other cases, such as o-dimethyltoluidine, a condensing agent (zinc chloride) may be required.<sup>2</sup> It has been found also that tribromaniline does not condense with formaldehyde, either under ordinary conditions, or in a sealed tube at 250°. The effect of the substituent bromine-atoms in this case is so strong that the action of an excess of bromine upon a benzol solution of anhydroformaldehydeaniline not only brominates the aromatic nucleus, but to a certain extent eliminates the methylene-group previously united with the nitrogen-atom. This is evidenced by the appearance of tribromaniline as a constant product of this bromination.

#### *A—Condensations of Formaldehyde and Aromatic Amines in Neutral or Alkaline Media.*

The essential reactions which may occur, depending upon the nature of the amine, and upon the relative proportions of amine and formaldehyde, are the following :



<sup>1</sup> *Annal.*, 302, 349.

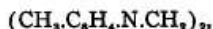
<sup>2</sup> *Alexander, Ber.*, 25, 2408 (1892).



### METHYLATION OF PARA-AMINOPHENOL

Compounds of these types are more or less generally referred to as "Schiff's Bases," which include also the condensation-products of other aldehydes.

The earliest known and simplest formaldehyde condensation of type (a) among aromatic amines was studied by Pratesi and Tollens<sup>3</sup> in the case of aniline. Anhydroformaldehydeaniline, or anhydroformaniline, is thus obtained in the trimeric form  $(C_6H_5N.CH_2)_3$ .<sup>4</sup> Polymerization occurs also with other amines, such as the toluidines<sup>5</sup> and p-aminophenol.<sup>6</sup> The existence of two forms of such compounds, having different melting points and solubilities, has been observed in several cases. This was attributed at first to different degrees of polymerization. It was shown by Bischoff, however, that  $(CH_3.C_6H_4.N.CH_2)_n$  exists in two forms, both of which have the same molecular weight, corresponding to the formula  $(CH_3.C_6H_4.N.CH_2)_3$ . He concluded that the two forms must be geometrical isomers of the *cis* and *trans* types with respect to the  $CH_3.C_6H_4$ -groups attached to the  $[=N.CH_2-]_3$  ring. Anhydroformaniline likewise probably exists in two forms. Dimeric forms of these anhydro-bases, such as



or structurally,  $CH_3.C_6H_4.N \begin{matrix} <CH_2 \\ > \\ <CH_2 \\ > \end{matrix} N.C_6H_4.CH_3,$

have been reported.<sup>7</sup>

The general reaction of which the formaldehyde-aniline condensation serves as a type was soon applied to the toluidines, etc., by Wellington and Tollens,<sup>8</sup> and has since that time been extended, where applicable, to apparently all amines of importance, both aliphatic and aromatic, as well as to many heterocyclic compounds.

<sup>3</sup> Pratesi, *Gazz. chim. ital.*, 14, 351 (1884); Tollens, *Ber.*, 17, 653 (1884); 18, 3309 (1885).

<sup>4</sup> Müller and Plöchl, *Ber.*, 25, 2020, (1892); Bischoff, *Ber.*, 31, 3248 (1899).

<sup>5</sup> Bischoff, *l. c.*

<sup>6</sup> D. R. P., 68707.

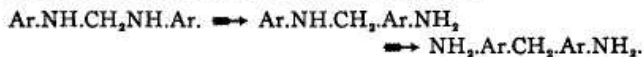
<sup>7</sup> *Ber.*, 31, 2037, 3248; *Annal.*, 256, 288.

<sup>8</sup> *Ber.*, 18, 3298 (1885).

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Condensation of two equivalents of amine and one of formaldehyde is of type (b), and yields methylene-di-imine compounds of the type-formula  $\text{Ar.NH.CH}_2\text{NH.Ar}$ . Thus two molecules of aniline and one of formaldehyde form methylenediphenyldi-imine, or dianilinomethane:<sup>9</sup>  $\text{C}_6\text{H}_5\text{.NH.CH}_2\text{NH.C}_6\text{H}_5$ . By boiling this compound in alcohol, it is transformed into anhydroformaniline.<sup>10</sup> Exactly analogous condensations occur with other amines.<sup>11</sup>

The most interesting reaction of the di-imine bases occurs when they are heated with amine-salts. Diamino-diphenylmethane derivatives are thus formed, by a rearrangement which recalls the transformation of hydrazobenzene to benzidine:<sup>12</sup>



As these compounds are formed directly when condensation is conducted in presence of free acid, and with base in excess of formaldehyde, the secondary reaction just given belongs more properly to Section B, where its probable mechanism will be indicated.

Condensations of types (a) and (b) may occur simultaneously, one or the other predominating; excess of aldehyde favors the first, while excess of amine favors the second.<sup>13</sup>

Condensations of type (c) are characteristic of secondary amines, and are in no essential manner different from the preceding. The methyltoluidines, for example, condense with formaldehyde to form  $(\text{C}_6\text{H}_7\text{.N.CH}_3)_2\text{CH}_2$ .<sup>14</sup> When heated with amine-salts, these compounds, like those obtained from primary amines, are rearranged to form dialkylamino-diphenylmethane derivatives.

Compounds intermediate between the methylene-di-imine bases ( $\text{Ar.NH.CH}_2\text{NH.Ar}$ ), and the diamino-diphenylmethanes

<sup>9</sup> Pratesi, Bischoff, *l. c.*

<sup>10</sup> Eberhardt and Welter, *Ber.*, 27, 1804 (1894).

<sup>11</sup> Eibner, *Annal.*, 302, 349 (1898); Bischoff, *l. c.*; Bischoff and Reinfeld, *Ber.*, 36, 41 (1903); D. R. P. 138393, etc.

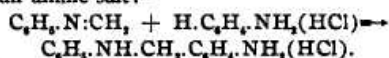
<sup>12</sup> D. R. P. 63081, 107718.

<sup>13</sup> Eibner; Eberhardt and Welter, *l. c.*

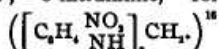
<sup>14</sup> Braun, *Ber.*, 41, 2145 (1908).

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(NH<sub>2</sub>.Ar.CH<sub>2</sub>.Ar.NH<sub>2</sub>), viz., the aminobenzylanilines (NH<sub>2</sub>.Ar.CH<sub>2</sub>.NH.Ar.), are formed when an anhydroformaldehyde-base is heated with an amine-salt:<sup>15</sup>



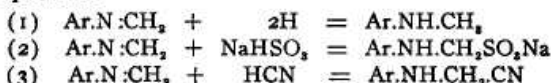
Condensations of nuclear-substituted amines proceed often in the normal manner; o-nitraniline, for example, yields



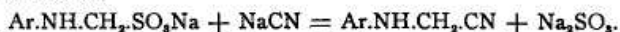
Similar condensations occur with halogenated amines, aminobenzoic acids, aminosulphonic acids, benzidine, tolidine, phenetidine, etc.

It is of great practical importance that the methylene-group of the diphenylmethane compounds can be condensed with a third amine-molecule by oxidation, forming triphenylmethane derivatives, among which fuchsine and the homologous pararosanilines are included.<sup>17</sup>

Primary condensation-products of the type Ar.N:CH<sub>2</sub>, although probably cyclic polymers devoid of double bonds, are able to unite, by addition, with several substances, the most important of which are (1) hydrogen, (2) sulphurous acid or bisulphites, and (3) hydrocyanic acid. These additions occur according to the following equations:<sup>18</sup>



The bisulphite compound contains a replaceable -SO<sub>3</sub>H or -SO<sub>3</sub>Na group:<sup>19</sup> by interaction with cyanide a phenylglycinenitrile results:



The synthesis of phenylglycine and its homologues is thus possible

<sup>15</sup> D. R. P. 87934.

<sup>16</sup> Pulvermacher, *Ber.*, 25, 2764; 26, 955.

<sup>17</sup> D. R. P. 53937, 55565, 61146, 67013, 73092.

<sup>18</sup> Miller and Piöchl, *Ber.*, 25, 2020 (1892); Eibner, *Annal.*, 316, 89 (1901); Lepetit, *Atti. accad. Lincei*, 26, I, 126 (1917); *Gazz. chim. ital.*, 47, I, 197 (1917); *C. A.*, 1918, 366.

<sup>19</sup> Knoevenagel, *Ber.*, 37, 4073 (1904).