suggested that the formation of these products depends upon a selective action of the Grignard reagent on the initial products of the reaction.

2-Chlorobenzylmagnesium chloride and 2,6-dichlorobenzylmagnesium chloride have been prepared and their behavior toward certain reactants has been investigated. The tendency of these reactants to yield products of rearrangement appears to decrease in the following order: acetyl chloride > acetic anhydride > methyl chlorocarbonate > carbon dioxide.

The mechanism of the rearrangement process in abnormal reactions of benzylmagnesium chloride is discussed.

ITHACA, NEW YORK

REDUCTION STUDIES OF SCHIFF BASES. I. THE REDUCTION OF METHYLENE-PARA-AMINOPHENOL AND ITS PROBABLE STRUCTURE

BY E. C. WAGNER

Schiff bases of the simple type $RCH=NR'$,[1] when of relatively high molecular weight, are apparently not polymerized, and can in many cases be hydrogenated to the corresponding secondary amines.[2] With bases obtained from aldehydes of low molecular weight, notably formaldehyde, polymerization occurs, and may be the cause of difficulties in reduction. Polymerization has been demonstrated for compounds such as methylene-aniline, methylene-toluidines, and ethylidine-aniline.[3] That a reversible relationship may exist among monomeric and polymeric forms was suggested by early investigators,[4] and was made to appear very probable by the work of Ingold and Piggott.[5] No account of the polymerization of these bases appears in the recent review by Carothers.[6]

Cyclic structures of the type (A) were assigned to certain polymeric

[1] These and the corresponding ketone derivatives may be called the azomethines: Möhlau, *Ber.*, **31**, 2250 (1898).

[2] See, e. g., German Patent 211,869; Wheeler, THIS JOURNAL, **35**, 976 (1913); Shepard and Ticknor, *ibid.*, **38**, 381 (1916); Kaufmann and Müller, *Ber.*, **51**, 126 (1918); Skita and Keil, *ibid.*, **61**, 1452 (1928); Zechmeister and Truka, *ibid.*, **63**, 2883 (1930); Buck, THIS JOURNAL, **53**, 2192 (1931).

[3] Tollens, *Ber.*, **18**, 3309 (1885); Miller and Plöchl, *ibid.*, **25**, 2020 (1892); **29**, 1462 (1896); Pulvermacher, *ibid.*, **25**, 2762 (1892); Bischoff, *ibid.*, **31**, 3248 (1899).

[4] (a) Tollens, *ibid.*, **17**, 653 (1884), and Ref. 3; (b) Wellington and Tollens, *ibid.*, **18**, 3298 (1885).

[5] Ingold and Piggott, *J. Chem. Soc.*, (a) **121**, 2381, 2793 (1922); (b) **123**, 2745 (1923).

[6] Carothers, *Chem. Reviews*, **8**, 353–426 (1931).

Schiff bases by Bischoff,[3] Löb,[7] and Goecke,[8] on the basis of rather slight experimental evidence, though Miller and Plöchl[3,9] had pointed out the possibility of geometric isomerism for such compounds, and Bischoff[3] obtained two forms of methylene-*p*-toluidine which seemed to be so related, and whose existence was consistent with a ring structure. The study of the formation and thermal cleavage ("division") of certain compounds containing the 1,3-dimethinediazidine ring has in Ingold's laboratory yielded more substantial evidence for the ring structure of at least dimeric bases.[5][10] To a few dimeric bases Miller and Plöchl[3] and their students[11] were led by chemical evidence to assign somewhat doubtful open-chain formulas, *e. g.*, for ethylidine aniline: $C_6H_5N=CHCH_2CH(CH_3)NHC_6H_5$.
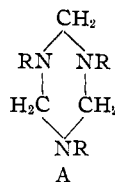
Reduction of Schiff bases has been used rather frequently as a method of alkylation, and occasionally to obtain indications as to their structure. Due to the present lack of definite information with respect to the course of aldehyde–amine condensations in acid media,[12] the results obtained by reduction can be interpreted in terms of structure probably only for Schiff bases formed in absence of acids.

Application of reduction to the problem of structure proof, as here proposed and exemplified below, involves these steps: (1) to show by molecular weight determinations that the Schiff base polymerizes, (2) to reduce the base strongly and identify and determine as completely as possible the products, and (3) to ascertain approximately the extent to which hydrolysis may interfere, so that formation of primary amine by reduction can be recognized if it occurs.

The results of a molecular weight determination may not be decisive, for the degree of polymerization may be determined in part by the solvent used, the temperature. etc.   The influence of solvent is shown below in the case of methylene-*p*-aminophenol; that of temperature is inferable upon comparison of the results obtained for methylene-*p*-toluidine by Bischoff and later by Ingold and Piggott.[13]   The determination of molecular weight,

[7] Löb, *Z. Elektrochem.*, **4**, 428 (1898).

[8] Goecke, *ibid.*, **9**, 470 (1903).

[9] Miller and Plöchl, *Ber.*, **27**, 1281 (1894).

[10] Ingold, *J. Chem. Soc.*, **125**, 87 (1924); **127**, 1141 (1925).

[11] Eibner, *Ber.*, **27**, 1296 (1894); *Ann.*, **318**, 58 (1901); **328**, 121 (1903); **329**, 210 (1903); Eibner and Purucker, *Ber.*, **33**, 3658 (1900); *cf.* Simon, *Ann. chim. phys.*, [7] **9**, 433 (1896); German Patents 376,013, 491,856.

[12] Though condensation in acid media has been variously reported to follow some special course, there seems to be in the literature evidence that the initial product, obtained in presence or absence of acid, is the simple azomethine, perhaps in hydrated form   A careful study of the course of condensation in acid media seems to be needed.

[13] Bischoff, *Ber.*, **31**, 3253 (1899); Ingold and Piggott, Ref. 5b.   Bischoff found the compound to be trimeric in boiling benzene. Ingold and Piggott found it to be dimeric in freezing benzene, and monomeric at 250° (Victor Meyer method).

however, and especially if made in solvents indifferent with respect to association or the reverse, may at least show whether or not the base is capable of polymerization.

Reduction of Schiff bases is often complicated by hydrolysis, which is more pronounced with acid agents, and which regenerates the original amine and aldehyde.[4b,14] This may lead to secondary interference if the reduction is prolonged, for the regenerated aldehyde may condense with the hydrogenated base.[15] In order to minimize or avoid hydrolysis during reduction the most practical devices seem to be (1) to reduce in absence of water,[16] (2) to condense in presence of the reducing agent, i. e., to reduce the nascent base,[17] or (3) to reduce the preformed base very rapidly, so that hydrolysis is put into disadvantageous competition with hydrogenation, as was done in the work described below.

The possible products of the reduction of a Schiff base will be determined by its structure. Simple azomethines (RN=CHR′) yield typically secondary amines. Alkylidene-diimines [(RNH)₂CHR′], which would yield primary and secondary amines, can be excluded from consideration if the amine and aldehyde condensed are of simple types,[18] and if excess of aldehyde is used.[14b] Compounds such as Bischoff's dimers, whose structure is doubtful, cannot well be considered in this connection, as their cleavage by reduction has not been reported. Cyclic polymerides, however, such as $ArN\overset{CH_2}{\underset{CH_2}{\diagdown}}NAr$, should yield as products of reduction *primary*, *secondary* and *tertiary* amines. To the reduction products named

[14] (a) O. Fischer, *Ber.*, **19**, 748 (1886); (b) Anselmino, *ibid.*, **41**, 621 (1908); (c) Skita and Keil[2]; (d) Langman, Healy and Dutt, *Quart. J. Indian Chem. Soc.*, **4**, 75 (1927); *Chem. Abstracts*, **21**, 2669 (1927); (e) Reddelien, *Ber.*, **48**, 1462 (1915); (f) Reddelien and Danilov, *ibid.*, **54**, 3132 (1921). Alkali is in some cases favorable to condensations: (g) Eberhardt and Welter, *ibid.*, **27**, 1804 (1894); (h) Bischoff and Reinfeld, *ibid.*, **36**, 41 (1903); (i) *cf.* Eibner, *ibid.*, **30**, 1444 (1897), and also (j) Wheeler and Smith, THIS JOURNAL, **41**, 1862 (1919).

[15] This perhaps accounts for the formation of a little dimethylaniline during the preparation of methylaniline by Frankland, Challenger and Nicholls [*J. Chem. Soc.*, **115**, 198 (1919)], using Morgan's method. The results of secondary condensations during acid reductions cannot well be predicted [*cf.* Goldschmidt, *Chem. Z.*, **24**, 284 (1900); **26**, 606 (1902); **28**, 1229 (1904); German Patent 96,851].

[16] O. Fischer, *Ber.*, **19**, 748 (1886); Mailhe, *Bull. soc. chim.*, **25**, 321 (1919); **27**, 229 (1920).

[17] Morgan, U. S. Patent 1,221,077; Skita and Keil.[1]

[18] Primary amines with negative substituents may condense to yield diimine bases: Pulvermacher;[3] Wheeler and Weller, THIS JOURNAL, **24**, 1063 (1902); Wheeler, *ibid.*, **30**, 163 (1908); Wheeler and Jordan, *ibid.*, **31**, 937 (1909); Jordan, *ibid.*, **32**, 973 (1910); Wheeler and Smith, *ibid.*, **41**, 1862 (1919); Kühling, *Ber.*, **27**, 567 (1894). Secondary amines yield typically the diimine bases: Braun, *ibid.*, **41**, 2145 (1908). Tertiary amines: Pinnov, *ibid.*, **27**, 3166 (1894); Möhlau and Heinze, *ibid.*, **35**, 359 (1902); Braun and Kruber, *ibid.*, **45**, 2991 (1912).

must be added any aldehyde and amine regenerated by hydrolysis. It may be concluded that the formation of primary amine (in quantity exceeding that attributable to hydrolysis), of secondary amine, and especially of tertiary amine, all as reduction products of a Schiff base known to polymerize, collectively constitutes evidence of a cyclic structure.

Formation of tertiary amine has been reported in only a few cases,[7,8,15,19] and then under circumstances which made the structural implications ambiguous. Primary amine has been obtained rather generally, but has apparently been regarded hitherto exclusively as an hydrolysis product. That primary, secondary and tertiary amines may all be formed as major products of the reduction of a Schiff base is shown below for the compound methylene-p-aminophenol. The structures of some other bases will be tested similarly in work now in progress.

The Reduction of Methylene-p-aminophenol and its Structure.— Methylene-p-aminophenol, produced by condensation of p-aminophenol and formaldehyde in alkaline[20] or neutral solution, is stated to be a polymeride,[21,22] though apparently without determination of its molecular weight. The view of Feldman[23] that it is only an addition product is incompatible with experimental results to be given below. No evidence as to the structure of methylene-p-aminophenol has been available hitherto.

The *molecular weight* of methylene-p-aminophenol was determined by the freezing point method in phenol and in trimethylcarbinol. Four specimens were examined, the averaged values in phenol being 147, 179, 127, 124 (calculated for monomer, 121),[24] while in trimethylcarbinol there was obtained the much higher value 408. These results suggest that methylene-p-aminophenol can exist wholly or largely monomeric and that it can polymerize, though more or less indefinitely, and that the molecular weight is not independent of the solvent.[25] It follows that the molecular

[19] German Patents 376,013, 491,856, 503,113.

[20] German Patent 68,707; *Frdl.*, Vol. 3, p. 996.

[21] Beilstein–Prager–Jacobson, "Organische Chemie," 4th ed., Vol. 13, p. 452.

[22] Levi, *Gazz. chim. ital.*, **59**, 544 (1929).

[23] Feldman, *Giorn. chim. ind. applicata*, **7**, 406 (1925); *Chem. Abstracts*, **20**, 3452 (1926).

[24] The first two specimens were made from pure p-aminophenol hydrochloride in alkaline solution saturated with hydrogen. The third was a specimen made from pure p-aminophenol in alkaline solution saturated with nitrogen; *Anal.*: nitrogen (Kjeldahl), 11.29%; calcd., 11.57%. The fourth value represents material made by neutral condensation: excess formaldehyde was added to a cold saturated solution of p-aminophenol, with air replaced by nitrogen, the product separating in crystalline form; nitrogen, 11.33%.

[25] It is possible that the high molecular weight in tertiary butyl alcohol was the result of association, though such solvents do not typically exert this influence [H. Meyer, "Analyse," 4th ed., J. Springer, Berlin, 1922, p. 417]. On the other hand depolymerization in phenol solution, while it has been observed for metacetaldehyde

weight in phenol or other solvent need not be that of the compound dissolved in acid for reduction. As appears below, the evidence of reduction indicates polymerization, perhaps by acid.[26] Experiments to test this for methylene-*p*-aminophenol were inconclusive.[27]

Reduction of Methylene-*p*-aminophenol.—Attempted reduction in alkaline media by various agents was not successful, as judged by absence of methyl-*p*-aminophenol separable as nitrosamine. Electrolytic reduction in acid solution,[28] using a lead cell of the type described by Lukens,[29] was in several trials partially effective, the best yield of methyl-*p*-aminophenol being 18%. Feldman[23] failed to hydrogenate methylene-*p*-aminophenol catalytically, but hydrogenation in alcohol and in presence of palladium has been claimed to give a good yield of secondary base.[30] Rapid and satisfactory reduction was effected by zinc dust and dilute sulfuric acid, both at about 20° and at higher temperatures.

To isolate the products of reduction, the liquid was made ammoniacal and extracted with ether in an automatic apparatus. During the extraction *p*-aminophenol crystallized from the ether in the boiling flask. As the methylated bases are freely soluble in ether, a useful and nearly complete separation of *p*-aminophenol present after reduction was thus very simply accomplished. The methylated bases were obtained from the ether extract by distillation under reduced pressure. They were weighed, dissolved in dilute acid, and in an aliquot part the secondary base was precipitated as nitrosamine and weighed. The dimethyl compound was either determined by difference, or was obtained from the nitrosamine filtrate, eventually by vacuum distillation. When necessary, *p*-aminophenol was identified as benzal-*p*-aminophenol (m. p. 185°, corr.); methyl-*p*-aminophenol as the nitrosamine (m. p. 135° corr.), or as the dibenzoyl derivative (m. p. 174° corr.); and dimethyl-*p*-aminophenol as the picrate (m. p. 170° corr.) or as the benzoate (m. p. 157–158°). Every isolation operation was separately examined as to accuracy, using weighed amounts of pure materials. The necessary corrections thus determined were relatively small, and are implicit in the results tabulated later.

In some of the reduction experiments it was possible to account for an average of 84% of the starting material in the form of recovered and identified products. As the work required for each complete experiment was somewhat prolonged, and involved a number of operations capable

[Hantzsch and Oechslin, *Ber.*, **40**, 4341 (1907)], would scarcely lead to different but reproducible values for different specimens of methylene-*p*-aminophenol.

[26] Law, *J. Chem. Soc.*, **101**, 154 (1912).

[27] Methylene-*p*-aminophenol recovered after treatment with acid showed increased molecular weight in phenol, but the material analyzed considerably too low for nitrogen.

[28] *Cf.* German Patent 143,197.

[29] Lukens, *J. Ind. Eng. Chem.*, **13**, 562 (1921).

[30] German Patent 437,975.

of only moderate accuracy, it is not certain whether the 16% unaccounted for may be attributed to manipulative deficiency or to presence of some undetected reaction product. It was found that the reduction of methylene-p-aminophenol yielded methyl-p-aminophenol and dimethyl-p-aminophenol in about equal amounts, and that over 25% of the p-aminophenol originally condensed was regenerated. It was important to this inquiry to know whether this p-aminophenol was formed from methylene-p-aminophenol by hydrolysis wholly or by hydrolysis and reduction jointly. Experiments were made to determine approximately the extent of hydrolysis under the conditions of reduction but in absence of the reducing agents.[31] It was found that at about 20° the hydrolysis by 30% sulfuric acid was 9% in thirty minutes; and at about 80° it was 27% in fifteen minutes. While it seems improbable that hydrolysis was equally extensive when in competition with vigorous reduction, the results obtained for reduction below 25° make unnecessary any assumption on this point. In these reductions about 25% of the p-aminophenol was regenerated, of which not over about 10% (and probably less) was due to hydrolysis. It may therefore be stated that the reduction products of methylene-p-aminophenol were p-aminophenol, methyl-p-aminophenol, and dimethyl-p-aminophenol (see Table).

This result cannot be reconciled with the structure $HOC_6H_4N=CH_2$, nor with the view that polymers are molecular aggregates of this unit, except by assumption of secondary condensations (following hydrolysis) and secondary reductions, for which there is at present no useful evidence. As suggested in the introduction, the formation of primary, secondary and tertiary bases, all as reduction products of methylene-p-aminophenol, permits the conclusion that polymerized methylene-p-aminophenol is a valency compound with a structure analogous to that previously assigned to methyleneaniline and methylenetoluidine, and containing the type of hetero-elementary ring for whose existence in certain Schiff bases Ingold obtained experimental evidence of a different kind. For the simplest polymer this structure is

$$HOC_6H_4N \underset{CH_2}{\overset{CH_2}{\diagup\diagdown}} NC_6H_4OH$$
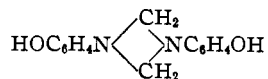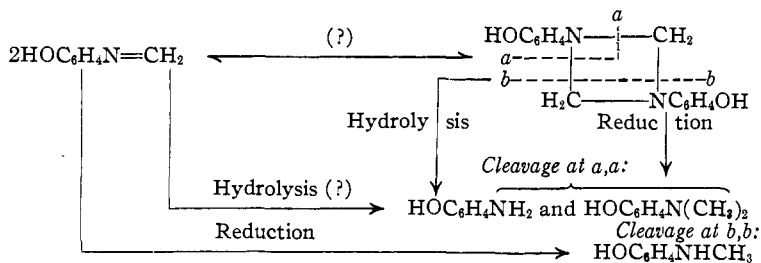
which, as well as higher polymers of like structure, could yield by reduction the products obtained.

The experimental facts, including the possibly labile relationship between monomer and polymers, the hydrolysis of both, and their reduction to

[31] The extent of the condensation was determined in an aliquot part, and the rest of the solution treated with acid. After suitable treatment to remove unhydrolyzed methylene-p-aminophenol (or its acid alteration product), the total p-aminophenol present was recovered and weighed as benzal-p-aminophenol.

the three bases obtained, may be presented diagrammatically as follows, using for simplicity the dimer:

$$2HOC_6H_4N=CH_2 \xleftarrow{\quad (?) \quad}$$

$$
\begin{array}{c}
a \\
HOC_6H_4N\text{---}|\text{---}CH_2 \\
a\text{----}|\text{----} \\
b\text{----}|\text{----------}|\text{----}b \\
H_2C\text{--------}NC_6H_4OH
\end{array}
$$

Hydroly | sis   Reduc | tion

Cleavage at a,a:

Hydrolysis (?) → $HOC_6H_4NH_2$ and $HOC_6H_4N(CH_3)_2$

Reduction

Cleavage at b,b:

$HOC_6H_4NHCH_3$

Experimental

(1) Chemicals

p-Aminophenol.—For most of the work there was used the hydrochloride, purified by several crystallizations from hot approximately 6 *N* hydrochloric acid. *p*-Aminophenol base, used for preparation of pure methylene-*p*-aminophenol for analysis and molecular weight determination, was obtained from the pure hydrochloride, which was dissolved in water and the base precipitated by addition of saturated sodium sulfite solution. The product was crystallized from hot water, all the operations of recrystallization including the filtration being conducted with air replaced by nitrogen, and was dried *in vacuo*.

Formaldehyde.—There was used Baker's "c. p." solution, filtered, and assayed by the method of Romijn.

Phenol.—(1) A lot made from aniline was purified by distillation and by three partial freezings, the product melting at 41.2° corr. (2) Merck's phenol was distilled through a short packed column, the end fractions being discarded. The material boiled at 182.4° corr., and melted at 40.9° corr.

Trimethylcarbinol.—The Eastman product was purified by three partial freezings.

(2) Apparatus.

The outfit used in the condensation and reduction experiments was assembled in such manner as to permit all operations, up to the reduction itself, to be conducted in absence of air, which was excluded by flooding the entire closed system with nitrogen. The condensing vessel was an Erlenmeyer flask whose stopper carried two small separatory funnels, one for formaldehyde and the other for sodium hydroxide solution, as well as an inlet and an exit tube. Connections were so made that a single stream of nitrogen could be passed in series through all the liquids used before any of them were mixed. The precipitating apparatus consisted of a liter three-necked flask provided with a liquid-seal stirrer, a dropping funnel for dilute acetic acid, and a graduated separatory funnel for aliquotting. Sufficient water was put into the flask to afford suitable dilution of the condensation liquid before precipitating the methylene-*p*-aminophenol, and connections were so made that nitrogen from the exit tube of the condensing unit was passed in series through the graduated funnel, the water in the precipitation flask, and finally the acetic acid.

(3) Procedure for Condensation and Reduction

Condensation.—In a typical experiment 25 g. of *p*-aminophenol hydrochloride was dissolved in 100 cc. of water in the condensing flask, 15 cc. of 36% formalin put into one separatory funnel and about 35 cc. of 40–50% sodium hydroxide solution into the other. The precipitation flask contained 250–300 cc. of water, and the acid funnel contained 6 *N* acetic acid. The whole system was flooded with nitrogen by passing

a rapid stream of the gas for about an hour. The condensation flask was immersed in an ice-bath, enough alkali solution was admitted to dissolve the aminophenol as phenolate, and after allowing the solution to cool the formaldehyde was added rapidly, and condensation allowed to proceed for two hours with chilling and with a slow stream of nitrogen passing. The entire liquid was then forced into the measuring funnel; to do this it was necessary to change one rubber tubing connection and to invert the condensing flask, when pressure of nitrogen effected the transfer. The flask was washed out with water saturated with nitrogen, the washings were transferred also, and the liquid in the measuring funnel was mixed.

To determine the extent of the condensation an aliquot part (*e. g.*, one-fifth) of the liquid was admitted to the precipitating flask. While operating the stirrer rapidly, dilute acetic acid was introduced by drops until precipitation was complete. The separated methylene-*p*-aminophenol was filtered, washed, dried *in vacuo* and weighed. To determine the *p*-aminophenol which escaped condensation, the slightly acid filtrate was shaken with a small excess of benzaldehyde, and the precipitated benzal-*p*-amino-phenol[32] filtered off and weighed. The extent of condensation usually exceeded 80%; the highest yield recorded was 94%. The reaction was found to be not sensitive to changes in conditions, hence detailed data for numerous experimental condensations are omitted.

Reduction.—The measuring funnel, containing the main body of the condensation liquid, was withdrawn, the end of the stem passed below the surface of 60% sulfuric acid (a volume equal to that of the alkaline liquid) in a large beaker, and the solution was allowed to flow into the acid, the funnel being kept filled with nitrogen until it was empty and had been washed with water. Simultaneously with the introduction of the condensation liquid into the acid the addition of zinc dust was begun (a weight equal to that of the aminophenol salt), and was continued as rapidly as possible, the selected reduction temperature being maintained by cooling or heating, and the mixture mechanically stirred. Reduction was continued until nearly all the zinc had dissolved (about thirty minutes), but was probably complete long before this point was reached. Numerous experiments in which the conditions or the procedure were modified showed the reduction to be rather unresponsive to such changes.

(4) **Isolation of the Products of Reduction.**—The reduction liquid was poured into a mixture of chipped ice and strong ammonium hydroxide taken in moderate excess. The alkaline liquid was extracted with ether in a modified Schwarz "perforator."[33] After twelve to fifteen hours' extraction the *p*-aminophenol was filtered from the ether extract and weighed. The methylated bases were obtained from the ether solution by distillation under reduced pressure.[34] The mixed bases were weighed, and then dissolved in dilute sulfuric acid. An aliquot part of this solution was chilled in ice and treated with 25% sodium nitrite solution, and the precipitated nitrosamine was filtered off, washed sparingly with ice water, dried *in vacuo*, and weighed. In some experiments the dimethyl-*p*-aminophenol left in the nitrosamine filtrate was isolated finally by distillation under reduced pressure and weighed as base;[35] in others it was deter-

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[32] Haegele, *Ber.*, **25**, 2753 (1892); German Patent 208,434.

[33] Houben, "Die Methoden der organischen Chemie," 3d ed., G. Thieme, Leipzig, Vol. I, 1925, p. 571. This useful apparatus was improved by introduction of a stirrer with liquid seal, and with paddles in the water and the ether layers opposed, so as to obtain a sliding interface.

[34] The boiling range of the mixture was about 157°_{15} to 165°_{18}. A prepared mixture of about equal parts of monomethyl- and dimethyl-*p*-aminophenol boiled at 160°_{18} to 162°_{20}.

[35] The yield of dimethylaminophenol thus found was decreased due to the fact that this compound is in some way reactive with nitrous acid, with evolution of gas.

mined by difference, its presence being shown by precipitation of the picrate. These methods of estimating the methylated bases were much better than the attempted separation of their sulfates, as used in earlier work.

The results of a number of complete experiments are presented in the table.

TABLE I

RESULTS FOR SOME EXPERIMENTS ON FORMATION OF METHYLENE-p-AMINOPHENOL IN ALKALINE SOLUTION, AND ITS REDUCTION BY ZINC DUST AND SULFURIC ACID

Condensation			Reduction						
Yield,[a] %	Not condensed,[b] %	Total, %	Temp. of reduction, °C.	p-a. p. recovered after reduction, %	p-a. p. recov.[j] from hydr. and redn., %	Mixed methylated bases, %	Monomethyl p-a. p., %	Dimethyl-p-a. p., %	Total p-a. p., accd. for, %
76.8[c]	23.0	99.8	50–83	25.6	2.6 (?)	33.8[e]	24.4[f]	16.8[e]	66.8
.. [c]	..	...	45–88	35.9	..	43.5[e]	..	..	79.4
.. [c]	..	...	45–84	36.8	..	..	37.1[f]	..	73.9
85.8[d]	16.3	102.1	60–80	20.2	3.9 (?)	..	18.4[e]	20.6[e]	60.1
76.8[d]	21.4	98.2	80–85	26.0	4.6 (?)	..	23.6[f]	22.5[g]	74.8
88.8[d]	15.5	104.3	70–90	26.1	10.6	..	27.0[f]	22.0[g]	75.1
93.9[d]	5.6	99.5	70–90	35.3	29.7	40.4[g]	19.7[j]	20.7[h,i]	75.7
.. [d]	8.2	...	Below 25	35.5	27.3	56.3[g]	30.8[f]	25.7[h,i]	92.0
.. [d]	13.7	...	Below 21	37.2	23.5	47.3[g]	21.8[f]	25.3[h]	84.3
Average of last three	9.2		36.0	26.8	48.0	24.1	23.9	84.0

[a] Precipitated from an aliquot and weighed. [b] Precipitated and weighed as benzal-p-aminophenol. [c] Condensation at room temperature. [d] Condensation in ice-bath. [e] Separated and weighed as sulfate. [f] Separated and weighed as nitrosamine. [g] Isolated by distillation *in vacuo* and weighed as base. [h] Determined by difference. [i] Presence of dimethyl-p-aminophenol established by isolation of picrate. [j] Total p-aminophenol recovered after reduction minus that present due to failure to condense.

(5) **Methylene-p-aminophenol and Some Derived Compounds.**—Only a few observations believed to be new are appended.

Methylene-p-aminophenol.—Made in absence of alkali this compound was obtained as a crystalline precipitate. When made in presence of alkali and subsequently precipitated, it is an amorphous powder, practically white if made and isolated in an air-free system, but otherwise more or less discolored. In the air it darkens and finally becomes resinous. Methylene-p-aminophenol is insoluble in water, but dissolves in alkali (the solution darkens promptly in air), in ethyl and other alcohols, in phenol and aniline, and in dilute hydrochloric or sulfuric acid. The freshly prepared solution in acid appears to contain methylene-p-aminophenol, but on standing or heating some of the compound suffers hydrolysis, and some is rendered resinous and insoluble by secondary changes not yet explained. At present no method of purification is known, and no satisfactory test of purity is available, as the compound has not been found to be recrystallizable from any solvent tried, and has no determinable melting point. The specimens used for analysis and for molecular weight determinations were therefore prepared from pure materials and under such conditions that the isolated product would be as pure as possible.

Dimethyl-p-aminophenol Picrate.—This useful identifying derivative for the tertiary base has apparently not been reported hitherto. It was obtained by addition of sodium acetate to the slightly acid solution, and then an excess of saturated aqueous picric acid. On standing and chilling, the picrate separated as glistening yellow crys-