Their formula would make retene an 8-methyl-6-isopropylphenanthrene. They offer no better evidence for their formula than Bamberger and Hooker did for formula I. They state that the formula is in accordance with the oxidation products, 1,2,4-benzenetricarboxylic- and metaphthalic acids! The very formation of these acids, however, is conclusive evidence against the formula, for such a compound would not yield the above acids. Their assumption is also shown to be untenable by the work described in this paper. It does explain the low esterification velocity of the acid, but many other arrangements would do just as well.

It may be pointed out that the formula (III), which has now been proved for retene, has *one* position (1-) diortho-substituted and if abietic acid is really a carboxyl derivative, the acid group might be in this position. The very extensive literature is so contradictory that one can not rely on it to decide this point. Some consider the abietic acid to be a dihydroxy derivative and others even question the composition, $C_{19}H_{28}O_2$, of the acid.

The wide bearing of the work, on retene, on natural products is still further shown by the suggestion of Neuberg and Rauchwerger that cholesterol is related to abietic acid and may therefore contain a reduced retene nucleus.

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THE COLORED SALTS OF SCHIFF'S BASES.

III. THE SALTS OF BASES FORMED BY CONDENSING *m*-AMINODIMETHYLANILINE AND *m*-AMINODIETHYLANILINE WITH AROMATIC ALDEHYDES.

BY F. J. MOORE.

Received January 19, 1910.

It has already been shown in previous papers[1] that benzylidene compounds of the general type,

when treated with acids in non-aqueous solvents, add successively two molecules of the latter, and that the salts containing one molecule of acid differ markedly in color from those containing two molecules. The former are, for the most part, dark red, while the latter are light yellow, the free bases themselves varying from a light cream color to orange. For this behavior three possible explanations have been suggested. For a detailed discussion of these, the reader must be referred to the papers mentioned. Here it will be sufficient to sum them up briefly as follows:

The first ascribes the difference in the color of the salts to the position of that nitrogen atom selected by the first molecule of acid. The second

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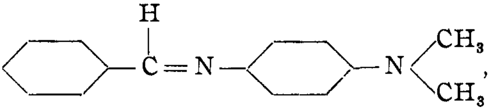
[1] THIS JOURNAL, 30, 394 and 1001.

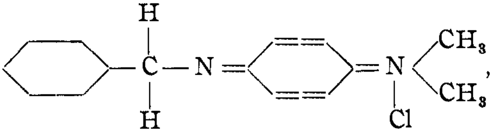
assigns to the dark-colored salts a quinoid constitution, regarding the compounds of lighter color as benzoid. The third assumes the potential existence of stereoisomeric red and yellow bases and salts, whose relationship to each other is akin, perhaps, to that of the isomeric unsymmetrical oximes.

The work described in the present paper was undertaken with the intention of testing the second of these explanations, which regards the dark-colored substances as quinoid. In accordance with this hypothesis, the addition of hydrochloric acid to benzylidene-*p*-aminodimethylaniline, for example, would cause transformations such as are illustrated by the following series of formulae:

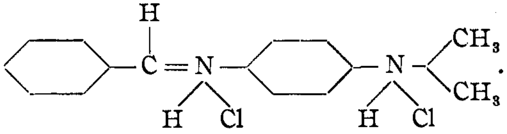
(1)



(2)



(3)



A convenient method of testing this hypothesis would consist in preparing analogous compounds which, from their structure, could not readily assume a quinoid constitution, and testing the results of salt formation in these cases. Now it is well-known that *p*-quinones form with considerable readiness, whereas *o*-quinones are more difficult to prepare, and *m*-quinoid substances are not known with certainty.[1] Applying this reasoning to the case in hand, it might be argued that the bases previously used in the course of this investigation might well form quinoid salts, since they all had their two nitrogen atoms in *p*-position to each other. It might, however, be confidently expected that the analogous *m*-compounds could not do this. Should these bases, when prepared, show a behavior with acids which was different from that of the *p*-compounds, then it might well be concluded that the dark-colored salts of the latter were quinoid. Should the *m*-compounds, on the other hand, show the same behavior as the *p*-compounds, then one of two possible conclusions might be drawn: either that the dark-colored salts of the *p*-compounds were not quinoid, or else that *m*-quinones may be formed more readily than any other evidence has thus far led us to believe.

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[1] Compare R. Meyer, *Ber.*, 41, 2437; Zincke and Schwabe, *Ber.*, 42, 797; R. Meyer and Desamari, *Ber.*, 42, 2809.

The compounds first selected for the experimental investigation were the products formed by condensing *m*-aminodimethylaniline with aromatic aldehydes. The reaction takes place readily and smoothly. When the products were treated with hydrochloric acid in ethereal or benzene solution, all the salts formed proved to be light in color, the shade not being markedly different, whether base or acid was in excess. The greatest difference of this kind was shown by the condensation product with cinnamic aldehyde, which gave a decidedly redder precipitate when acid was in excess, than under the reverse conditions. It will be noticed that this behavior was entirely different from that of the corresponding *p*-compounds. On its face, this would seem to indicate that the dark-colored salts of the latter were quinoid. Unfortunately this argument is a good deal weakened by the curious physical properties of the bases themselves.

While the *p*-compounds crystallize beautifully from alcohol and other organic solvents, and have sharp melting points which make them useful for the identification of aldehydes, the condensation products of *m*-aminodimethylaniline with aldehydes have properties which are the reverse of all this. They are typically amorphous, they crystallize from no solvent yet tried, and they have no melting point, but soften gradually on heating. They are, for the most part, very soluble in benzene, and on evaporation of this solvent, they are left as transparent resins which show no signs of crystallization even after months of standing. The products form readily when aldehyde and amine are mixed, and the yield is good. Side-reactions do not seem to take place, and when pains are taken to purify the products as far as possible, the analytical results agree well with the formulae derived from the method of preparation. Apparently then, the properties just described must belong to the compounds as such, although, of course, the usual criteria of purity are lacking. These properties would seem to indicate that the substances concerned were polymers, and if this were the case, the possibilities of constitution which have been thus far discussed might have little bearing. It seemed desirable to test this point by means of molecular weight determinations. Freezing-point measurements were therefore attempted in both benzene and diphenylamine. The substance chiefly studied was benzylidene-*m*-aminodimethylaniline, because it was believed that the sample used was purer, perhaps, than any of the other bases. A series of tests was, however, made with each of the other compounds. The results were discordant and unsatisfactory, the numbers obtained sometimes differing among themselves by a figure corresponding to a whole unit formula. Nevertheless the sum total of the results would seem to show that the bases were not high polymers. Speaking generally they indicate that in 0.5 per cent. solution, the bases were bimolecular. The association seemed to increase with increasing concentration, and in a 2 per cent. solution, the compounds appeared to have a molecular weight three or four times that represented by the simple formula. These results cannot be called satisfactory or conclusive, but are, perhaps, as much as can be expected from materials whose purity and homogeneity is open to so much question.

Since in any case the results above described gave no satisfactory solution to the original problem, *m*-aminodiethylaniline was prepared and condensed with five of the more common aldehydes. These compounds, in their turn, showed the same properties which have been already described as characteristic of the methyl compounds. They, too, are amorphous waxes or gums, and their salts are, for the most part, of light color, whether one or more molecules of acid are added.

Although both these bases have proved a disappointment so far as that problem is concerned for the solution of which they were originally prepared, yet their uniformly amorphous character when compared with the crystalline nature of the isomeric *p*-compounds suggests that their study might throw some light upon the fundamental differences which exist between the *m*- and *p*- relationships in di-substituted benzene derivatives. It is hoped to extend this study further in the future.

Experimental Part.

The *m*-aminodimethylaniline used in this investigation was prepared by the method of Groll[1] from dimethylaniline. The directions are easy to follow, and the product obtained is of satisfactory purity. When distilled in hydrogen, it boils with perfect constancy at 267° to almost the last drop.

From the literature, it is easy to get the impression that the aminodimethylanilines are unstable compounds. This is not the case, but they are extremely sensitive to the oxygen of the air. Indeed they turn black and grow tarry even on standing a few days in a well-stoppered bottle. If, however, they are distilled in hydrogen, and then the connections are hermetically sealed without allowing any access of air, no deterioration takes place. Samples which were treated in this way have been preserved in this laboratory for more than two years, and show no signs of change.

Benzylidene - m - aminodimethylaniline. — Molecular quantities of *m*-aminodimethylaniline and benzaldehyde were mixed. Condensation took place with a slight evolution of heat in the course of a few minutes, the mass becoming thick and pasty. To free the product from any possible excess of the amine or aldehyde, it was warmed several times with small portions of dilute alcohol (in which it is not very soluble), the pasty mass being constantly stirred to bring all parts of it into contact with the solvent. During this treatment, the substance assumes the

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[1] *Ber.*, **19**, 200 (1886).

consistency of a thick paste which can be drawn out like molasses candy into long golden-yellow strings. After several treatments of this kind, the substance grows hard and brittle on cooling. When this point had been reached, it was pulverized and washed with cold dilute alcohol. Finally, enough cold 95 per cent. alcohol was employed to bring the residue into solution, and this solution was poured into a large quantity of cold water. This causes a milky turbidity, but if a little sodium chloride solution is added, the substance is precipitated in flocks, which may then be rapidly filtered by suction and washed repeatedly with cold water. This latter method of purification was twice repeated, and the product finally dried in vacuum. It was now a light yellow mass which retained hardly any odor of benzaldehyde, and when pulverized was extremely electric. No crystalline form could be observed in this product, and all attempts to find a solvent from which it would crystallize have proved fruitless. Nevertheless the following results of analysis seem to show that the substance was essentially pure benzylidene-*m*-aminodimethylaniline.

Calculated for $C_{15}H_{16}N_2$:	C, 80.30;	H, 7.19;	N, 12.52.
Found:	79.97;	7.20;	12.69.

Condensation Products with Other Aldehydes.—*m*-Aminodimethylaniline was also condensed with anisaldehyde, cinnamic aldehyde, and piperonal. All the products had essentially the same properties as that just described. For this reason, the details need not be repeated. Purification was also carried out in the same manner where this was possible, but the method of dissolving in alcohol and precipitating by water did not work well in the cases of the cinnamic aldehyde and piperonal compounds. It is therefore probable that these compounds were not as pure as the others. This is also borne out by the results of analysis. Only nitrogen determinations were made in these cases.

Anisylidene-m-*aminodimethylaniline*: Calculated for $C_{16}H_{11}ON_2$, N 11.05; found, 10.91.

Cinnamidene-m-*aminodimethylaniline*: Calculated for $C_{17}H_{18}N_2$, N 11.23; found, 9.96.

Piperonylidene-m-*aminodimethylaniline*: Calculated for $C_{16}H_{16}O_2N_2$, N 10.45; found, 9.04.

Derivatives of m-*Aminodiethylaniline.*—The *m*-aminodiethylaniline required was prepared essentially according to the suggestions of Groll[1] by nitrating diethylaniline and reducing the *m*-nitro compound. Groll's directions for the nitration and separation of the *m*- and *p*-products can hardly be improved. From reading his article, however, one gets the idea that the *m*-nitro compound can be distilled at ordinary pressure. Attempts made to do so in this laboratory yielded a

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[1] *Loc. cit.*

product much contaminated by water and some ill-smelling substance whose odor resembled that of pyridine. This nitro compound can however be obtained in a high state of purity by distilling with steam. At 100° this process is very slow and tedious, and the quantities of water required are so large as to render the subsequent ethering-out very laborious. Much better results are obtained when the flask containing the nitro compound is placed in an oil bath heated to 160° (thermometer in the bath) and superheated steam then blown through. In this way, no water condenses in the distilling flask, and a liberal quantity of very pure oil distils over rapidly. Small amounts of this nitro compound can be conveniently identified by the precipitate obtained at once when it is treated with picric acid in alcoholic solution. After a single crystallization from alcohol, this picrate melts at 138° (uncorrected).

Reduction to the amino compound proceeds very smoothly under the influence of tin and hydrochloric acid. The most convenient method of isolation is to pour the hot reduction mixture directly into an excess of concentrated caustic soda solution, warm a few minutes, cool with an equal quantity of ice, and shake out with ether. A second treatment with ether is superfluous. In this way, 75 grams nitro compound yielded 50 grams amine which, when distilled in hydrogen, boiled constantly at 277°. The freshly distilled base is as nearly colorless as freshly distilled aniline, and consequently somewhat purer than that described by Groll. Like other substances of its class it is very sensitive to the air, rapidly turning brown. Portions of it which are not intended for immediate use should therefore be at once sealed up in an atmosphere of indifferent gas. When an alcoholic solution of the base is mixed with picric acid, no precipitate forms at once, but after standing for some time, beautiful yellow prisms separate. These can be washed repeatedly with cold alcohol, and then recrystallized from the same boiling solvent. They then melt sharply at 152°.

Condensation Products with Aldehydes.—These compounds were prepared in the same manner as the analogous methyl compounds. A general account of their physical properties has already been given in the earlier portion of this paper. These properties made it so evident that no assistance could be obtained from them, in solving the question at issue, that no thorough study was made of them, and no analyses carried out. A brief account of their appearance and the color of their addition products with hydrochloric acid follows.

The condensation products with benzaldehyde and anisaldehyde are stiff, golden yellow gums. When they are dissolved in ether, and an ethereal solution of hydrochloric acid is added, the precipitate first thrown down is pale yellow. This becomes practically white when an excess of the acid is added.

The compound formed with cinnamic aldehyde is a brick-red pasty mass. It also is soluble in ether, and from this solution hydrochloric acid precipitates a flocky red salt.

The condensation product with piperonal is a greenish yellow slime. When hydrochloric acid is added to its solution in dry ether, the precipitate first formed is pale yellow. A little more acid changes this color to a light red, and an excess to a bright lemon-yellow.

The compound formed with vanillin is a dark, blood-red, transparent jelly. Hydrochloric acid precipitates yellow salts.

Summary.

The salts of bases formed by condensing *m*-aminodimethylaniline and *m*-aminodiethylaniline with aldehydes do not show the same peculiarities of color as the corresponding salts of the *p*-compounds.

From this the conclusion might be drawn that the dark-colored salts of the latter were quinoid, but the force of this argument is a good deal weakened by the probability that these *m*-bases are polymers.

The amorphous character of these compounds (perhaps due to polymerization) in contrast to the crystalline nature of the *p*-compounds suggests applications to the benzene problem which are worthy of future study.

The thanks of the writer are due to Mr. E. G. Genoud for much valuable assistance during the earlier portions of this work.

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THE ACTION OF MAGNESIUM UPON THE VAPORS OF ORGANIC COMPOUNDS.

BY EDWARD H. KEISER AND LEROY MCMASTER.

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In 1894 Edward H. Keiser and M. B. Breed[1] studied the action of metallic magnesium upon the vapors of some of the aliphatic alcohols and found that when the metal is heated in a tube through which the vapor of the alcohol is passing it soon begins to glow and after the action has ceased and the tube allowed to cool, a black residue is left. This residue when put into water evolves a gas slowly and on the addition of a few drops of ammonium chloride a more rapid evolution of gas is obtained. It was shown that the gas thus given off consisted of hydrogen mixed with small quantities of allylene.

In a subsequent paper by Edward H. Keiser[2] the work was continued, other alcohols and acetone were subjected to the action of magnesium, and it was shown that in every case the black residue gave off allylene when treated with water. The best yield of allylene was obtained from

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[1] *J. Franklin Inst.*, Dec., 1894.

[2] *Am. Chem. J.*, 18, 328.