All of our results show that the temperature of ashing below fusion is not so important a factor where only the percentage of ash is desired, but when determining the phosphorus as phosphoric acid in ash the greatest caution must be observed to keep the temperature below the volatilization point of the combined phosphorus.

LABORATORY OF VEGETABLE PHYSIOLOGICAL CHEMISTRY,
BUREAU OF CHEMISTRY,
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THE COLORED SALTS OF SCHIFF'S BASES.

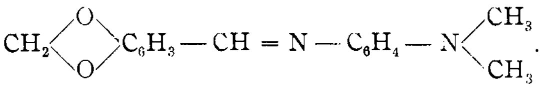
A Contribution to Our Knowledge of Color as Related to Chemical Constitution.

BY F. J. MOORE AND R. D. GALE.

Received January 6, 1908.

I. The Hydrochlorides of Bases Formed by Condensing *p*-Amino Dimethylaniline with Aromatic Aldehydes.

The starting point of the present investigation was a chance observation made upon the compound produced by condensing *p*-aminodimethylaniline with piperonal. This product is of a light orange color and has the formula



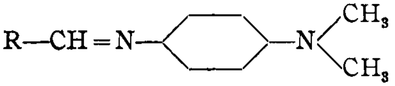
$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle \mathrm{C_6H_3-CH=N-C_6H_4-N}\left\langle\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right. .$$

When this substance, either in the dry state or in ethereal or benzene solution, is treated with dry hydrochloric acid gas, one molecule of the latter is first added to form a salt of a deep blood-red color. This salt can further add another molecule of the acid to form a dihydrochloride. The color of the latter salt, in sharp contrast to that of the former, is a bright lemon-yellow.

We found this phenomenon so striking that we determined to prepare a number of compounds of analogous constitution and study the color of their salts. The first substances selected were those most strictly analogous to the one already mentioned, namely, the condensation products of *p*-aminodimethylaniline with aromatic aldehydes. These bases furnish the subject matter of the present paper. They all show a behavior toward hydrochloric acid, and (so far as has been tested) also toward other acids, entirely analogous to that described in the case of the piperonal compound. A minor exception has to be noted in the case of anisaldehyde. When its condensation product with *p*-aminodimethylaniline is treated with hydrochloric acid, the same color changes are observed as in the other cases, but analysis of the products show that a maximum of nearly three molecules of the acid is here absorbed. This behavior will be discussed more fully in the experimental part.

Subsequent papers will deal with other compounds similarly constituted. Thus we have prepared a number of bases of this class by condensing aromatic aldehydes with *p*-aminodiethylaniline. Of these it may be said that as far as investigated, they show the same reactions toward acids as the corresponding dimethyl compounds. The salts are, however, less stable. One of us, in collaboration with Mr. R. G. Woodbridge, Jr., is also studying the bases formed by condensing *p*-aminodiphenylamine with aldehydes. These bases unite with one molecule of hydrochloric acid to form dark red salts like the monohydrochlorides already described. These salts, however, do not add a second molecule of the acid.

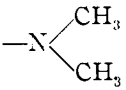
From the above it is clear that we are dealing with a quite general law which may be stated thus: Bases of the general formula



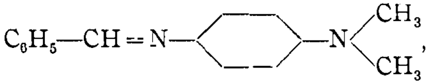
add hydrochloric acid to form salts of a dark red color (darker than that of the free base) while most of them also add another molecule of the acid to form salts of a light yellow color (usually lighter than that of the free base).

Before attempting a theoretical explanation of this uniform behavior, a word should be said concerning the color of the simpler benzylidene compounds containing only one atom of nitrogen. As aromatic aldehydes condense so readily with primary amines, a voluminous literature has grown up on the subject. We have not made an exhaustive study of this, but the general rule seems to be that neither such bases nor their salts are very highly colored. This certainly holds true of those which have come under our observation. Thus the condensation product of benzaldehyde with aniline is a pale cream color (perhaps due to a trace of impurity) and the product formed by treating piperonal with aniline is perfectly colorless. The hydrochloride of the piperonal compound is a bright lemon-yellow, that of the benzaldehyde compound a much paler shade, only slightly stronger than that of the free base. For purposes of comparison we have prepared several other condensation products of piperonal. All of these, namely the compounds prepared by treating piperonal with *p*-toluidine, *p*-chloraniline, *p*-bromaniline, *p*-aminoethylbenzoate, and *m*-nitraniline, all showed the same light color of base and salt.

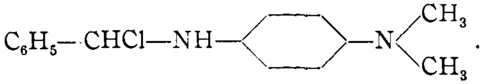
From this we can draw the conclusion that if the group —CH = N— is to be considered a chromophore at all, it is a weak one; certainly far weaker than —N = N—. Of the intensifying effect of acid addition or salt formation, whether we call it "auxochrome" effect or "halochromy," we may say that in this group of compounds it is noticeable but not striking.

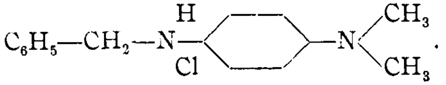
Turning back now to the more complicated bases containing two atoms of nitrogen, inspection of their formulae shows the presence of the substituted amino group,  which acts as an auxochrome in so many important dyes. The effect of this group is seen in the color of the bases which contain it. These colors range from a light yellow, through golden yellow, to a fairly strong orange. None go as far as deep red. The color of the salts has already been dwelt upon.

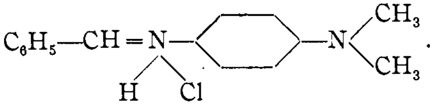
Our interpretation of the color relations so frequently referred to will depend upon our idea of exactly what happens when one molecule of hydrochloric acid is added to these bases. If we take for purposes of illustration the simplest case, that of benzylidene *p*-aminodimethylaniline,

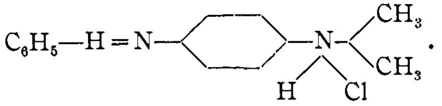


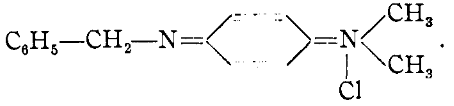
we can imagine hydrochloric acid being added to the compound in such different ways as to form products of any one of the following formulae:

(1) 

(2) 

(3) 

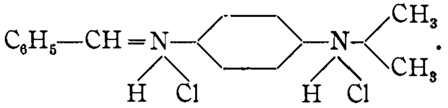
(4) 

(5) 

Of these, (1) and (2) seem hardly worthy of serious consideration. The addition products of acids to the simpler bases of this type, such as benzylidene aniline, $C_6H_5{-}CH{=}N{-}C_6H_5$, have always been looked upon as ammonium salts. They split at once under the influence of water into the corresponding aldehyde and the salt of the base from which they were originally formed, in this case, aniline hydrochloride and benzaldehyde. The salts of the more complicated compounds now under discussion act in a similar way. This would exclude (1). It would not necessarily exclude (2), according to which the addition products are to be looked upon as secondary chloramines. They are, however, rather more stable than chloramines would be expected to be, and they do not evolve chlorine when they are treated with hydrochloric acid. A more conclusive argument, however, against (1) and (2), and in favor of the salt-like character of the compounds is the fact that so far as tested (and only qualitative tests have thus far been made) sulphuric acid gives addition products entirely similar in color and properties to those formed by hydrochloric acid.

Formulae (3) and (4) represent more nearly what we should expect if the addition of hydrochloric acid is to be looked upon as simple salt formation. The formulae differ only in the nitrogen atom, which is supposed to become pentavalent. In deciding between them we have to remember that the simpler bases like piperonylidene aniline add one molecule of hydrochloric acid to form salts which are not dark red but light yellow. Now these salts must have their hydrochloric acid united to that nitrogen which forms part of the chain connecting the two benzene rings. It would therefore seem quite probable that these red salts have their hydrochloric acid bound differently. Furthermore, if we assign to the red salt the formula (4), a consistent and plausible explanation lies near at hand for the difference in color between the salts containing one and two molecules of hydrochloric acid respectively. In the first case, we have three factors coöperating to intensify the color, the chromophore group, —CH = N—, the auxochrome group, $N{<}\genfrac{}{}{0pt}{}{CH_3}{CH_3}$, and, finally, whatever influence in this direction is to be ascribed to salt formation—"halochromy."

Now the compound with two molecules of hydrochloric acid can hardly have any other formula than the following:



Here the nitrogen belonging to the chromophore group, —CH = N—, has changed its valence, and this might naturally be expected to prove destructive to the chromophore character of the group. Furthermore, the light yellow color of these saturated salts is in entire harmony with the similar color of the simpler bases which, as already pointed out, must have the hydrochloric acid upon the central nitrogen.

An argument against the explanation just outlined might be found in the hydrolysis of the salts. It is a well known fact that the salts of the simpler bases like benzylidene aniline decompose at once when treated with water, yielding, in this case, aniline hydrochloride and benzaldehyde. The salts of the more complicated bases we are studying react similarly, except that the operation takes place in two steps. If the yellow hydrochloride of piperonylidene *p*-aminodimethyl aniline, for example, be treated with water, it immediately turns dark red, obviously owing to the formation of the red monohydrochloride. The color then slowly fades out as this salt splits into the hydrochloride of *p*-aminodimethylaniline and piperonal. Now the weak spot in the hydrochloride of piperonylidene aniline is obviously the molecule of acid attached to the central nitrogen. If the red salt has then a constitution analogous to that shown in formula (4), it is not, at first sight, quite clear why it should hydrolyze at all. The above argument, however, against (4) does not seem as serious as that which can be brought against (3). If we give the latter formula to the red hydrochloride, we can only ascribe the intensity of its color to salt formation—halochromy. We should then expect a further intensification of the color when the second molecule of hydrochloric acid is added. As we have already seen, this is not the case.

There remains the quinoid formula, (5). This also offers a consistent explanation. We have only to assume that the red hydrochloride exists in the quinoid, the yellow dihydrochloride in the benzoid form. It seems at first a little difficult to account for the hydrolysis into aldehyde and amine salt on this basis, but the shifting of double bonds involved is not of a particularly revolutionary character. It would also seem possible that the dihydrochlorides might also exist in a quinoid form. Perhaps, when more compounds have been studied, such salts will be found. In the meantime, some work is under way in this laboratory designed to throw light upon the probability of a quinoid formula for the red hydrochlorides.

An explanation, differing from any of the above, has occurred to us since reading a recent article by Anselmino[1] which came to our notice after the experimental work described in this paper was practically completed. Anselmino found that when *p*-homosalicylic aldehyde is condensed with aniline the product formed exists in two different forms, a red and a yellow. That this is not simply a case of dimorphism is shown by the fact that the two forms differ in chemical behavior and give different derivatives. The most probable assumption concerning their constitution would seem to be that they are stereoisomeric in the same sense as the isomeric oximes of unsymmetrical ketones. If we try to explain the behavior of the compounds we are studying upon a similar basis, we should have to say that the salts vary in color because they are derived from different stereoisomeric bases, one red the other yellow. That in

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[1] Ber., 40, 3465 (1907); also *Ibid.*, 38, 3989 (1905).

the case of the bases themselves, the yellow form is alone stable; that when the bases add hydrochloric acid, the yellow salts first formed are unstable and go over to form salts of the other—red base. Finally, when the saturated salts are formed, that a transformation in the opposite sense takes place. This explanation disregards the question as to which nitrogen holds the hydrochloric acid. Now, in this connection, we have to remember that previous to this recent work of Anselmino, no well attested cases of stereoisomerism had been observed among benzylidene compounds, though they have long been looked for; and, further, that Anselmino himself observed no such isomerism in the case of the salts. In fact he points out that his red and yellow bases gave identical hydrochlorides. This, of course, is no conclusive argument against a stereochemical explanation of the facts which we have observed. It does, however, furnish a reason for not accepting such an explanation hastily.

It will be seen in the experimental part of this paper that the salts of salicylidene *p*-aminodimethylaniline undergo change in color on standing, and it has been already pointed out that compounds of this class containing the diethylamino group show similar behavior. From what has already been said, it will be seen in what a variety of directions, an explanation of this fact might be sought. Any discussion of these possibilities would, however, be premature until more work upon these ethyl compounds has been done. For the present also we wish to reserve any opinion as to the probable formulae of the red hydrochlorides.

Experimental Part.

The condensation product of *p*-aminodimethylaniline with benzaldehyde was first prepared by Calm.[1] It is interesting to note his observation that this base adds two molecules of hydrochloric acid to form a "white" salt. This illustates the light color of the saturated hydrochloride, and at the same time shows that Calm attached no significance to the formation of the red intermediate product. He gives a determination of chlorine in the saturated salt. The other bases studied in this paper were prepared by Nuth[2] at the suggestion of Calm. He did not prepare salts. We have little to add to his description of the bases, except for some melting points already corrected by more recent observers. We prepared the bases by mixing molecular quantities of the amine with the various aldehydes, sometimes warming a little on the water bath. The reaction then proceeded at once and gave good yields. The product was recrystallized once from alcohol. It was usually found that further recrystallization did not raise the melting-point. The bases range in color from a light yellow to a light orange.

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[1] Ber., 17, 2938 (1884).

[2] *Ibid.*, 18, 573 (1885).

In studying the salts, we at first allowed hydrochloric acid to act upon the bases in the dry state. When piperonylidene *p*-aminodimethylaniline, for example, is spread upon a piece of porcelain (a crucible cover) and a current of hydrochloric acid passed over it, the mass suddenly turns a deep red. This color no sooner appears than it begins again to fade, owing to the formation of the light yellow saturated salt. A similar effect is produced when the base is dissolved in dry ether and hydrochloric acid gas introduced. Here the liquid first turns dark red; then a precipitate of the same color appears, and, finally, the time varying with the amount of substance present, the color of the solution grows rapidly lighter in shade, the precipitate becomes bright yellow, and at the end, the supernatant liquid is colorless, the saturated salt being practically insoluble in ether. It will frequently be noticed that at the mouth of the tube where the gas enters, and where consequently the acid is always in excess, a yellow deposit of the dihydrochloride forms at once. This makes it probable that the red salt, however it is prepared, contains a good deal of the yellow enclosed. This shows itself in the analytical data furnished further on. When the salts were prepared for analysis, the following procedure was employed in order to avoid this kind of contamination as much as possible. First, the free base was dissolved in sodium-dried ether and then a solution of hydrochloric acid in dry ether was run in from a burette. When preparing the saturated salt, the addition of the acid solution was continued as long as any precipitate formed. To prepare an unsaturated salt, a little less than half as much acid was added as had been found necessary in preparing the saturated one. The precipitates so obtained were filtered by suction, washed repeatedly with dry ether, and finally dried in a vacuum desiccator containing both concentrated sulphuric acid and sticks of caustic soda. If lumps formed during the drying, these were ground up and the desiccation continued. As far as our observation goes, these salts melt only with decomposition, and the temperature observed depends largely upon the time of heating. In the case of the saturated salts, the point of decomposition lies quite close to 200° in almost all cases. The chlorine determinations were in all cases made by the Carius method. The salts precipitated and dried as above described were used for analysis without recrystallization. Alcohols would have been the only practicable solvents for this purpose, but some experiments made in this direction led us to fear the contaminating effects of hydrolytic action. As we have pointed out above, the salts were probably more or less contaminated with each other, and perhaps, also with the free bases. Under the circumstances, we have not thought it desirable to make a large number of determinations, in the hope that some of them might agree more closely with the results of theoretical computation. In spite of the wide divergence to be observed in many cases, we think that the numerical results make plain the one point which we wish to emphasize at this time, namely, that the light colored salts contain about one molecule of acid more than the dark ones. The results follow:

Benzylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{15}H_{16}N_2HCl$, Cl, 13.60; found, 17.01. Saturated hydrochloride: calculated for $C_{15}H_{16}N_2.2HCl$, Cl, 23.09; found, 20.48.

Cinnamylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{17}H_{18}N_2HCl$, Cl, 12.36; found, 15.33. Saturated hydrochloride: Calculated for $C_{17}H_{18}N_2.2HCl$, Cl, 21.95; found, 21.34.

Piperonylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{16}H_{16}O_2N_2HCl$, Cl, 11.63; found, 15.19. Saturated hydrochloride: calculated for $C_{16}H_{16}O_2N_2.2HCl$, Cl, 20.78; found, 21.12, 21.05.

Salicylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{15}H_{16}ON_2HCl$, Cl, 12.81; found, 13.07. Saturated hydrochloride: calculated for $C_{15}H_{16}ON_2.2HCl$, Cl, 22.65; found, 22.47.

The color of the salts seemed less permanent in this case than in any we had previously studied. Nuth records that the free base turns red on standing in the air, and we notice that the red hydrochloride has a tendency to grow lighter in color. What is perhaps more curious is that the saturated hydrochloride which, when first precipitated, is almost colorless, grows considerably darker in color. We have since met with even more marked changes of this kind in the study of the bases formed by condensing *p*-aminodiethylaniline with aldehydes. We consider any theoretical discussion of this phenomenon to be premature until these diethyl compounds have been more thoroughly studied. The fact should be borne in mind, however, that, according to Anselmino, salicylic acid is one of those which forms isomeric aniles, one red, the other yellow.

Anisylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{16}H_{18}ON_2HCl$, Cl, 12.20; found, 12.20. $C_{16}H_{18}ON_2.2HCl$, Cl, 21.68; found, 18.34. Saturated hydrochloride: calculated for $C_{16}H_{18}ON_2.3HCl$, Cl, 29.27; found, 28.78, 26.16, 26.61.

In view of the fact that in the case of the red hydrochlorides high results for chlorine are usually obtained, probably owing to the tendency of these salts to enclose some of the saturated compounds, the numerical results given above leave it a little in doubt whether the red salt, in this case, contains, when pure, one or two molecules of acid. It is quite evident, however, that the saturated salt contains nearly three molecules. This seems to be one of those cases referred to by Baeyer[1] where a base shows itself capable of combining with more acid than its formula accounts for. It might be supposed that in both salts the additional molecule of hydrochloric acid attached itself to the methoxyl group to

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[1] Ber., **38**, 1157 (1905).

form an oxonium salt. This may be the correct explanation, but it is not necessarily so; for we find that the most simply constituted member of the whole group, benzylidene aniline, though it conains but one nitrogen and no oxygen, yet adds two molecules of hydrochloric acid, as shown by the following analysis:

Calculated for $C_{13}H_{11}NHCl$, Cl, 16.29; for $C_{13}H_{11}N.2HCl$, Cl, 27.90; found, 27.68, 27.62.

We were much surprised at this result, as it raised the question whether all of the benzylidene compounds containing one nitrogen might not behave similarly, and whether in those containing two atoms, all of the acid might not be held by one nitrogen. The analyses of the salts of the three following compounds, however, show that the addition of more molecules of acid than there are nitrogen atoms in the base, is the exception; though from what has gone before, it may well be of more frequent occurrence than has hitherto been supposed.

Piperonylidene Aniline.—This base was first prepared by Lorenz.[1] It is absolutely colorless, the first of these compounds which we have been able to prepare in that condition. The hydrochloride is bright yellow, and this makes perhaps the most striking example of simple "halochromy" which we have observed in the group. The hydrochloride contains but one molecule of acid, as is shown by the following analytical data:

Calculated for $C_{14}H_{11}O_2NHCl$, Cl, 13.55; found, 13.76, 13.51.

Piperonylidene p-Toluidine.—This substance crystallizes from alcohol in cream-colored prisms which melt at 98°.

Calculated for $C_{15}H_{13}O_2N$, C, 75.26; H, 5.48; N, 5.87. Found, 75.28; 5.55, 6.11.

The hydrochloride is light yellow. The percentage of chlorine was determined. Calculated for $C_{15}H_{13}O_2NHCl$, Cl, 12.86; found, 13.03, 12.98.

Piperonylidene p-Chloraniline,—The base melts at 78°. It has not been analyzed. It forms a light yellow hydrochloride. Calculated for $C_{14}H_{10}O_2NCl.HCl$. Cl, 23.95; found, 23.43.

We wished to learn something of the color of salts analogous to those formed by condensing aldehydes with *p*-aminodimethylaniline, but which contained an amino group not substituted by alkyl radicles. We had some hopes that at least a small yield of such compounds might be obtained by condensing one molecule of aldehyde with one of a diamine. Accordingly we treated piperonal with *p*-phenylenediamine, and also with benzidine. In both cases the only products we obtained were those formed by the condensation of one molecule of diamine with two molecules of piperonal. These bases are soluble with difficulty in alco-

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[1] Ber., 14, 792 (1881).

hol, ether, or the aromatic hydrocarbons. They can be crystallized from nitrobenzene, from which they separate in bronze yellow scales of a semi-metallic luster. The compound with *p*-phenylenediamine melts at 216°. Calculated for $C_{22}H_{16}O_4N_2$: C, 70.94; H, 4.33; N, 7.55. Found, 70.30, 4.52, 7.90.

The compound formed by condensing benzidine with piperonal melts not quite sharply at 241°. The liquid formed is not transparent, and it is possible that it is crystalline in character, as liquid crystals are not infrequently met with among compounds of similar constitution. The composition of the base was verified by a nitrogen determination. Calculated for $C_{28}H_{20}O_4N_2$, N. 6.50; found, 6.43.

We add some incomplete data concerning some substances prepared during the present investigation, but which, as they have no further theoretical interest for us, will probably not be worked with further.

Piperonylidene p-Aminoethylbenzoate.—This substance was prepared by condensing piperonal with *p*-aminoethylbenzoate. The base melts at 109°, is almost colorless, and forms a yellow hydrochloride.

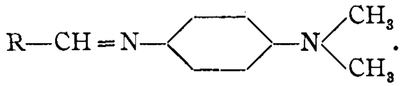
Calculated for $C_{17}H_{15}O_4N$, C, 68.64; H, 5.09; N, 4.72. Found, 68.34, 5.08, 4.84.

Piperonal condenses readily with *m*-nitraniline to form a base which melts at 119°. This forms a yellow hydrochloride. We have a nitrogen determination in the free base. Calculated for $C_{14}H_{11}O_4N_2$, N, 10.35; found, 10.56.

Piperonal condenses with *p*-bromaniline to form a product melting at 109°. This forms a hydrochloride of a light canary-yellow color. We have analyzed neither the base nor the salt.

Summary.

When *p*-aminodimethylaniline is treated with aromatic aldehydes, condensation products are formed which have the general formula



$$R—CH=N—C_6H_4—N\begin{matrix}CH_3\\CH_3\end{matrix}.$$

These bases add one molecule of hydrochloric acid to form dark red salts of a much deeper color than the free bases. The addition of more hydrochloric acid produces salts of a light yellow color, lighter than that of the free base.

Three explanations of this behavior are considered:

(1) That the first molecule of acid adds to the auxochrome nitrogen augmenting the color, while the second adds to the chromophore nitrogen, changing its valence and consequently destroying its chromophore character.

(2) That the monohydrochloride has a quinoid structure, while the saturated salt and the free base are benzoid.

(3) That there is a double series of stereoisomeric red and yellow bases and salts, the red form of the monohydrochloride being the stable one, the yellow form being stable in the other cases.

A decision as to which of these explanations is most applicable must be deferred until more experimental material can be collected.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
January 1, 1908.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

ON THE OXIDATION OF META-NITROBENZOYL CARBINOL.

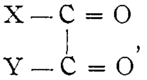
BY WILLIAM LLOYD EVANS AND BENJAMIN T. BROOKS.

Received January 15, 1908.

The work of Nef[1] on the oxidation phenomena exhibited by many series of organic compounds has made it possible to follow by experiment the exact course taken by such reactions. The recent work of Denis[2] on the behavior of various aldehydes, ketones and alcohols towards oxidizing agents is an excellent example of this kind of experimental study. In a previous paper by one of us,[3] it was shown that reactions of this type in the benzoyl carbinol series lend themselves admirably to this kind of treatment.

Zincke[4] and his students were the first to show that benzoyl carbinol, when acted upon by various oxidizing agents, gives mandelic, benzoylformic and benzoic acids in varying amounts according to the agents used. In a further study of this same substance by one of us,[5] it has been shown that benzoyl-formaldehyde is also one of the products of oxidation of benzoyl-carbinol. When benzoyl- formaldehyde is acted upon by alkalies,[6] and copper salts,[7] at 100°, it undergoes a benzilic acid rearrangement, giving mandelic acid exclusively. It has been shown by Denis that acetyl formaldehyde undergoes a similar rearrangement with dilute solutions of sodium hydroxide, and even with water alone at 100° it suffers a partial transformation.[8]

It is a well-known fact that many orthodicarbonyl compounds,



$$\begin{array}{c} X-C=O \\ | \\ Y-C=O \end{array},$$

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[1] Ann. Chem., **318**, 137; **335**, 191; **357**, 214.

[2] Am. Chem. J., **38**, 561.

[3] Evans, *Ibid.*, **35**, 115.

[4] Ber., **13**, 635; Ann. Chem., **216**, 311.

[5] *Loc. cit.*

[6] Pechmann, Ber., **20**, 2904; **22**, 2556.

[7] Evans, Am. Chem. J., **35**, 124.

[8] *Ibid.*, **38**, 584, 585.