helpful suggestions and much encouragement during the course of the investigation.

GÖTTINGEN.

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

THE OXIDATION OF METANITROBENZOYLFORMALDEHYDE.

BY WILLIAM LLOYD EVANS AND EDGAR JOHN WITZEMANN.

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In a previous report on the preparation and the oxidation of *m*-nitrobenzoylcarbinol[1] it was indicated that a study would be made of some of the substituted benzoyl carbinols for the following purposes: (1) to ascertain whether the same general course of reaction is followed as has been previously developed for this series of compounds[2] and (2) to discover what possible effect, if any, the introduction of substituents into the ring might have on these compounds towards oxidizing agents previously considered. This paper, which constitutes the second report on this work, deals solely with the preparation and the oxidation of *m*-nitrobenzoylformaldehyde. Briefly, the results of our experiments are as follows: (1) *m*-nitrobenzoylformaldehyde can be isolated as an actual oxidation product from *m*-nitrobenzoyl carbinol by means of copper acetate; (2) *m*-nitrobenzoylformaldehyde with potassium permanganate, potassium permanganate and sodium hydroxide, potassium ferricyanide and sodium hydroxide, freshly precipitated silver oxide and sodium hydroxide, freshly precipitated mercuric oxide and sodium hydroxide, yields *m*-nitrobenzoic acid exclusively; (3) both freshly precipitated silver oxide and mercuric oxide in the absence of an alkali were not reduced at room temperature by *m*-nitrobenzoylformaldehyde; (4) at 100° both of the reagents mentioned in (3) reacted in the same manner as the reagents in (2), *i. e.*, to give *m*-nitrobenzoic acid; (5) *m*-nitrobenzoylformaldehyde with hot aqueous solutions of copper acetate undergoes the benzilic acid rearrangement giving *m*-nitromandelic acid; (6) with alkalies the aldedyde undergoes the same rearrangement.[3] From the experiments on *m*-nitrobenzoyl carbinol previously reported and also from those herein given, the following conclusions may be drawn: (1) *m*-nitrobenzoyl carbinol and *m*-nitrobenzoylformaldehyde follow the same general course of reaction as the corresponding non-substituted compounds; (2) the two nitro-substituted compounds are more sensitive to reagents in the presence of alkalies; (3) there is a more general tendency for the oxidation reactions to progress to the benzoic acid (*i. e.*, *m*-nitrobenzoic acid) stage in the case of the two nitro-substituted compounds rather

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[1] Evans and Brooks, THIS JOURNAL, **30**, 404.

[2] Evans, *Am. Chem. J.*, **35**, 115.

[3] Nef, *Ann.*, **335**, 271, 272; **357**, 215, 231, 299, 302, 305, 308, 309.

than to give the possible intermediate substances, *i. e.*, *m*-nitromandelic acid and *m*-nitrobenzoylformic acid.

Experimental Part.

Preparation of m-Nitrobenzoylformaldehyde. (a) *m-Nitrobenzoylcarbinol and Copper Acetate.*—It has previously been shown[1] that benzoyl carbinol, when subjected to the mild oxidizing action of cold aqueous solutions of copper acetate and also copper sulfate, yields benzoylformaldehyde-monohydrate, which is identical in every respect with the synthetic substance obtained by Von Pechman.[2] In some preliminary experiments made previously[3] on the action of copper salts on *m*-nitrobenzoyl carbinol, an oil was obtained which did not react with Fehling's solution even after prolonged boiling, and which, with phenylhydrazine, gave a beautiful yellowish red crystalline product. These experiments have been repeated as follows: to three grams of *m*-nitrobenzoyl carbinol (1 mol.) dissolved in 300 cc. of water was slowly added a solution of 9 grams (3 mols.) of copper acetate dissolved in 150 cc. of water. The reaction mixture became turbid immediately and in the course of 30 minutes a considerable quantity of cuprous oxide had separated out. After having stood two weeks at room temperature to ensure completeness of reaction, the yield of red cuprous oxide was found to be 1.3 grams (theory = 1.17 grams). The ether solution, which was obtained by extracting the filtrate from the cuprous oxide 12 times with ether and drying the same with sodium sulfate, yielded a thick, viscous, straw-yellow oil having the mild characteristic odor of benzoylformaldehyde monohydrate. In order to remove the acetic acid present, the oily residue was dissolved in 25 cc. of water and the resulting solution was then treated with one gram of calcium carbonate. After having stood 12 hours with frequent stirring, the aqueous filtrate from the calcium carbonate was extracted with ether five times, the moist ether extract after drying as above yielding 2.7 grams of *m*-nitrobenzoylformaldehyde (theory = 2.96 grams).

(b) *ω-Monobromo-m-nitroacetophenone.*—To 10 grams of ω-monobromo-*m*-nitroacetophenone suspended in 500 cc. of water were added 6.9 grams (1 mol.) of silver nitrate. After boiling the mixture for two hours under a reverse condenser, the silver bromide was filtered off, the filtrate being immediately treated with calcium carbonate as in the preceding experiment. After extracting with ether and drying, a yield of 6.0 grams (theory 7.3 grams) of *m*-nitrobenzoylformaldehyde was obtained. It was found that by long-continued boiling an increasing amount of *m*-nitrobenzoic acid was produced. The same general results were obtained by the use of lead nitrate instead of silver nitrate.

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[1] *Am. Chem. J.*, **35**, 121–123.

[2] *Ber.*, **22**, 2557.

[3] Evans and Brooks, THIS JOURNAL, 30, 408.

Properties of m-Nitrobenzoylformaldehyde.—*m*-Nitrobenzoylformaldehyde as obtained in these experiments is a straw-yellow, slow-flowing oil. On long standing it becomes more viscous until it seems to be almost solid. After standing for four months, a sample of the most carefully prepared specimen did not exhibit the slightest tendency to crystallize. This property is identical with the dehydrated benzoylformaldehyde described by Von Pechmann.[1] Numerous attempts were made to crystallize the substance from the usual organic solvents and mixtures of them but without success. *m*-Nitrobenzoylformaldehyde does not form a monohydrate, nor can it be distilled without decomposition even at reduced pressure. It does not reduce Fehling's solution or ammoniacal silver nitrate solution.

Identification of m-Nitrobenzoylformaldehyde.—Owing to the extremely viscous nature of *m*-nitrobenzoylformaldehyde it was found inconvenient to analyze it. The two following methods were employed in its identification: (1) by converting it into the osazone and comparing this with the osazone formed from *m*-nitrobenzoylcarbinol; and (2) by converting it into *m*-nitromandelic acid. It was found most convenient to handle the substance for measurement in an ether solution, the oily residue obtained therefrom being dissolved subsequently in water.

(a) *Preparation of m-Nitrobenzoylformaldehyde Osazone from m-Nitrobenzoyl Carbinol.*—The method employed was an adaptation of Laubmann's method[2] for preparing the osazone of benzoyl carbinol, except that the *m*-nitrobenzoyl carbinol was used instead of previously preparing the hydrazone. A solution of one gram of *m*-nitrobenzoyl carbinol in the minimum amount of warm 50 per cent. alcohol was added to a warm concentrated solution of 4 grams of phenylhydrazine hydrochloride and 5 grams of fused sodium acetate in 50 per cent. alcohol, the reaction mixture being immediately heated in a sealed tube for four hours at 100°. The weight of the beautiful dark red needle-like crystals (which filled the tube), on allowing the tube to cool in the furnace over night after washing with 50 per cent. alcohol and drying, was 1.2 grams. This substance, after crystallizing three times from boiling benzene, gave a sharp melting point of 223° and analyzed as follows:

Calculated for $C_{20}H_{21}N_5O_2$: C, 66.98; H, 4.50; N, 19.59
Found: C, 66.45; H, 4.90; N, 19.74, 19.56

(b) *Preparation of m-Nitrobenzoylformaldehyde Osazone from m-Nitrobenzoylformaldehyde.*—One gram of *m*-nitrobenzoylformaldehyde, prepared by the action of copper acetate on *m*-nitrobenzoyl carbinol as described above, was dissolved in 25 cc. of water and to this solution 3 grams of phenylhydrazine were added. The dark-red oil, which was formed

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[1] *Loc. cit.*

[2] *Ann.*, 243, 246.

at first, was converted to a friable chalk-like mass on continued heating. This substance, when purified as in the preceding experiment, was found to be identical in every respect with the osazone obtained by the reaction of *m*-nitrobenzoyl carbinol and phenylhydrazine. The procedure described in this experiment was repeated on the oils obtained by the reaction of silver and lead nitrates on ω-monobromo-*m*-nitroacetophenone, the result in each case being an osazone identical with the one described. Two and one-half grams of a neutral oil obtained from the action of aqueous copper sulfate on three grams of *m*-nitrobenzoyl carbinol yielded with 3.00 grams of phenylhydrazine by this method a product which was identical in every respect with the osazone above described. These experiments prove, therefore, the identity of these oils to be *m*-nitrobenzoylformaldehyde.

m-Nitromandelic Acid from m-Nitrobenzoylformaldehyde.—(*a*) As is well known benzoylformaldehyde undergoes the benzilic acid rearrangement when acted on by aqueous solutions of the alkalies[1] and also of copper salts at 100°[2] forming *dl*-mandelic acid. As is shown above, *m*-nitrobenzoyl carbinol with copper acetate at ordinary temperature gives *m*-nitrobenzoylformaldehyde. Owing to its extreme sensitiveness towards caustic alkalies, the simultaneous formation of *m*-nitrobenzoylformaldehyde and its rearrangement were accomplished by a study of the behavior of *m*-nitrobenzoyl carbinol towards copper acetate at 100°. To a solution of two grams of *m*-nitrobenzoyl carbinol in 300 cc. of water was added a solution of 8.64 grams of copper acetate dissolved in 250 cc. of water. The reaction mixture, which showed almost immediately by its change of color that reduction was taking place, was heated to boiling for four hours. The residue, consisting of cuprous oxide and copper *m*-nitromandelate, weighed 3.38 grams. The filtrate, which was obtained by boiling this residue for some time with water, showed no reaction with ammonium hydroxide, thus showing the insolubility of copper *m*-nitromandelate and the absence of copper acetate. In order to obtain the weight of the copper *m*-nitromandelate, it was found most convenient to remove the cuprous oxide from the residue by levigation and finally 2.12 grams (theory = 2.50 grams) of the salt and 1.10 grams of the red cuprous oxide were obtained. The solution which was obtained by dissolving the salt in 70 cc. of dilute hydrochloric acid (1 : 3.33) was extracted with ether 6 times. The combined ether extracts after drying yielded 1.73 grams (theory = 1.84 grams) *m*-nitromandelic acid, (m. p. = 118°). The amount of *m*-nitromandelic acid demanded by theory from the amount of *m*-nitrobenzoyl carbinol used was 2.17 grams, the amount obtained being therefore 80 per cent. From these results it was expected

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[1] Von Pechmann, *Ber.*, 22, 2557. Evans, *Am. Chem. J.*, 35, 122.

[2] *Am. Chem. J.*, 35, 124.

that *m*-nitromandelic acid would react with copper acetate to form an insoluble copper salt. One gram of crystallized copper acetate dissolved in 25 cc. of water was added to a solution of one gram of *m*-nitromandelic acid in 25 cc. of water. The green salt, which began to separate almost immediately in the cold and was subsequently separated completely by boiling for 2.5 hours, was identical with the one found by the action of copper acetate and *m*-nitrobenzoylcarbinol. Yield = 1.14 grams (theory = 1.15 grams).

(*b*) When *m*-nitrobenzoylformaldehyde was tested with caustic alkalies it yielded *m*-nitromandelic acid which contained varying amounts of *m*-nitrobenzoic acid. This same behavior has been previously noted with lime and benzoylformaldehyde.[1] A solution of three grams of *m*-nitrobenzoylformaldehyde in 75 cc. of water was made slightly alkaline with 1.2 grams of sodium hydroxide. When this reaction mixture was worked up in the usual way, 2.05 grams of a yellow oil were obtained, which solidified on the addition of a trace of pure *m*-nitromandelic acid. For the reason above stated, the melting point was found to be 111°–113°, which was raised by the addition of the pure compound.

The Oxidation of *m*-Nitrobenzoylformaldehyde.

m-Nitrobenzoylformaldehyde and Potassium Permanganate.—When benzoylformaldehyde is oxidized by potassium permanganate, benzoic acid is formed exclusively, while in the presence of alkalies benzoylformic and benzoic acids are formed.[2] The substituted aldehyde gives *m*-nitrobenzoic acid exclusively with potassium permanganate alone, and also in the presence of sodium hydroxide as is shown by the following experiments. A solution of 4.44 grams (3 mols.) of potassium permanganate, dissolved in least amount of water, was added to 1.57 grams (1 mol.) of *m*-nitrobenzoylformaldehyde dissolved in 250 cc. of water. With very gentle warming and frequent shaking of the mixture for 24 hours, reducing the excess of potassium permanganate with a few drops of ethyl alcohol, and working up in the usual way, a yield of 0.87 gram (theory = 1.4 grams) of *m*-nitrobenzoic acid was obtained. Since *m*-nitrobenzoylformic acid and *m*-nitromandelic acid give *m*-nitrobenzoic acid exclusively when treated with sodium hydroxide and potassium permanganate,[3] it was expected that *m*-nitrobenzoylformaldehyde would yield the same product. That this proved to be the case was shown as follows: To 1.56 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 250 cc. of water was added a mixture of 2.76 grams (2 mols.) of potassium permanganate and 0.70 gram (2 mols.) of sodium hydroxide. The reaction mixture, after standing at room temperature for 48 hours, yielded 0.94 gram (theory = 1.39 grams)

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[1] *Am. Chem. J.*, 35, 123.

[2] *Ibid.*, 35, 128, 129.

[3] THIS JOURNAL, 30, 409.

of *m*-nitrobenzoic acid. Owing to the extreme sensitiveness of the aldehyde towards reagents (see above), slight amounts of tar were formed in these two experiments.

m-Nitrobenzoylformaldehyde, Potassium Ferricyanide and Potassium Hydroxide.—In striking contrast to the behavior of benzoyl carbinol and benzoylformaldehyde towards alkaline potassium ferricyanide[1] is that of *m*-nitrobenzoylcarbinol and *m*-nitrobenzoylformaldehyde, the non-substituted compounds giving mandelic acid while the substituted compounds give *m*-nitrobenzoic acid. To a solution of 1.63 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 200 cc. of water was added an aqueous solution of 9 grams (3 mols.) of potassium ferricyanide and 1.85 grams (5 mols.) of sodium hydroxide. After standing at room temperature, the reaction mixture yielded by the usual treatment 1.05 grams (theory = 1.58 grams) of *m*-nitrobenzoic acid.

m-Nitrobenzoylformaldehyde and Silver Oxide.—*m*-Nitrobenzoyl carbinol, when acted upon by silver oxide in the presence or absence of alkalies, gives *m*-nitrobenzoic acid, a result which is in accord with the action of the same reagents on benzoyl carbinol and the results obtained by Denis on acetol.[2] Since in the following experiments it will be shown that *m*-nitrobenzoylformaldehyde under either condition gives *m*-nitrobenzoic acid exclusively, it is perfectly evident therefore that *m*-nitrobenzoylformaldehyde, in the presence of silver oxide and sodium hydroxide, does not undergo the benzilic acid rearrangement before oxidation, but it must previously have dissociated into *m*-nitrobenzaldehyde and carbon monoxide, and these compounds then in turn were oxidized:

$$NO_2.C_6H_4.CO.CHO \longrightarrow NO_2.C_6H_4.CHO + CO$$

This interpretation of the reaction is in harmony with the results obtained by the oxidation of the corresponding carbinol, which possesses the possibility of dissociating as follows:

$$1.\ NO_2.C_6H_4.CO.CH_2OH \longrightarrow NO_2.C_6H_4.CO.CH \genfrac{}{}{0pt}{}{\nearrow}{\searrow} + HOH$$

$$2.\ NO_2.C_6H_4.CO.CH_2OH \longrightarrow NO_2.C_6H_4CHO + H_2CO$$

Thus, it is seen that in the presence of alkalies the *m*-nitrobenzoylmethylene formed in (1) possesses the possibility of being oxidized to *m*-nitrobenzoylformaldehyde, which substance would then oxidize as herein indicated.[3] It is interesting to note here that the bivalent carbon derivative in (1) possesses the possibility also of polymerizing and forming the derivatives of benzoylmethylene prepared by Paal and his students.[4] Paal interprets the formation of the tribenzoylcyclotrimethylene[5] upon the basis

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[1] *Am. Chem. J.*, 35, 127.

[2] Denis, *Am. Chem. J.*, 38, 579.

[3] Compare Nef, *Ann.*, 335, 191.

Paal and Schulze, *Ber.*, 33, 3784; 35, 168. Nef, *Ann.*, 335, 251.

Ber., 36, 2425.

of the existence of bivalent carbon derivatives first proposed by Nef. It is apparent that in the absence of alkalies, the oxidation of *m*-nitrobenzoyl carbinol could proceed through equation (2). The freshly precipitated and well washed silver oxide obtained from 5.01 grams (2.2 mols.) of silver nitrate was added to 1.17 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 200 cc. of water. No reduction having taken place after standing at room temperature for 48 hours, the reaction mixture was kept at the temperature of the boiling water-bath for several hours, whereupon reduction took place, as was evident from the deposit of metallic silver on the sides of the flask. After separating the silver oxide and soluble silver salts from the metallic silver by means of ammonium hydroxide, and working up the filtrate in the usual way, there was obtained 0.78 gram (theory = 1.11 grams) of *m*-nitrobenzoic acid.

Similarly 1.39 grams (1 mol.) in 200 cc. of water were tested with a mixture of 0.61 gram (2.1 mols.) of sodium hydroxide and the freshly precipitated and well washed silver oxide obtained from 7.18 grams (2.5 mols.) of silver nitrate. The same general phenomena were observed as in the preceding experiment. The reaction mixture yielded 0.95 gram (theory = 1.29 grams) of *m*-nitrobenzoic acid.

m-Nitrobenzoylformaldehyde and Mercuric Oxide.—Equal in interest to the preceding experiments are those with mercuric oxide alone and with sodium hydroxide. *m*-Nitrobenzoyl carbinol is analogous to benzoyl carbinol in its behavior towards these reagents, in that it gives *m*-nitrobenzoic acid exclusively. Since it is herein shown that *m*-nitrobenzoylformaldehyde does not undergo oxidation with mercuric oxide alone, it must be concluded that *m*-nitrobenzoyl carbinol in oxidizing must dissociate in the presence of this reagent as indicated in (2) above. To a solution of 1.49 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 200 cc. were added 2.23 grams (1.25 mols.) of freshly precipitated and well washed mercuric oxide. After standing at room temperature for 48 hours and finally heating for some hours on the water-bath, no reduction was observed. The reaction mixture was found to contain no *m*-nitrobenzoic acid. In the presence of alkali, the result was the same as that obtained by the use of silver oxide and sodium hydroxide. Since *m*-nitromandelic acid is unacted on by this reagent, it is obvious that the mechanism of the oxidation of the aldehyde with mercuric oxide and sodium hydroxide must be the same as with silver oxide and sodium hydroxide. To a mixture of 0.5 gram (2 mols.) of sodium hydroxide and 2.23 grams (1.25 mols.) of mercuric oxide covered with water were added 1.48 grams of *m*-nitrobenzoylformaldehyde in 200 cc. of water. Reduction took place almost immediately and the reaction went to completion without the addition of heat. The reaction mixture yielded 0.92 gram (theory = 1.16 grams) of *m*-nitrobenzoic acid. It is of considerable interest to note the difference in behavior of the two aromatic aldehydes herein considered, and of methyl glyoxal (pyruvic aldehyde) towards silver and mercuric oxide in the presence of sodium hydroxide. Denis[1] found that with methyl glyoxal the benzilic acid rearrangement is practically not affected by the presence of the oxide of mercury or silver, while the two aromatic aldehydes give practically no other substance than the benzoic acid. In the case of benzoylformaldehyde with silver oxide and sodium hydroxide a trace of mandelic acid was obtained[2] but the main product was an almost quantitative yield of benzoic acid. In conclusion we wish to thank Mr. Evan Mahaffey, of this laboratory, for the carbon and hydrogen determinations of the osazone analysis given above.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

THE PREPARATION OF TRIBASIC PHENOLPHTHALATES.

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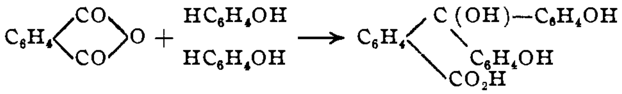
Introduction.

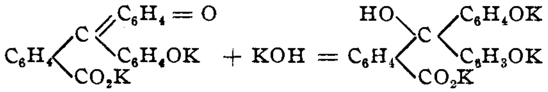
When Baeyer[3] heated phenol and phthalic anhydride in the presence of sulfuric acid, he did not obtain phenolphthalic acid as follows from the equation,



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + \begin{matrix}HC_6H_4OH\\HC_6H_4OH\end{matrix} \longrightarrow C_6H_4\left<\begin{matrix}C(OH)-C_6H_4OH\\ \diagdown\ C_6H_4OH\\CO_2H\end{matrix}\right.$$

but obtained a substance having one molecule of water less; namely, a lactone or anhydride, which is called phenolphthalein.

Phenolphthalic acid has not yet been prepared, and according to Baeyer it does not exist. Recently the fading of the phenolphthalein color, due to excess of alkali, has been ascribed to the formation of salts of phenolphthalic acid.[4]



$$C_6H_4\left<\begin{matrix}C\left<\begin{matrix}C_6H_4=O\\C_6H_4OK\end{matrix}\right.\\CO_2K\end{matrix}\right. + KOH = C_6H_4\left<\begin{matrix}(HO)C\left<\begin{matrix}C_6H_4OK\\C_6H_3OK\end{matrix}\right.\\CO_2K\end{matrix}\right.$$

We determined from the study of the fading velocity, that the colorless substance was the product of one molecule of alkali and one molecule of dibasic alkali phenolphthalein.[5] On determining the concentration of the reacting substance at equilibrium, we found that the result agreed with the following equation:

[1] *Am. Chem. J.*, 38, 585.

[2] *Ibid.*, 35, 131.

[3] Baeyer, *Ber.*, 4, 659 (1874).

[4] Green and Perkin, *J. Chem. Soc.*, 85, 389. Acree, *Am. Chem. J.*, 42, 122.

[5] Kober and Marshall, THIS JOURNAL, 33, 59 (1911).