

(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.

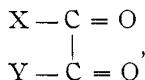
BY WILLIAM LLOYD EVANS AND BENJAMIN T. BROOKS.

Received January 15, 1908.

The work of Nef<sup>1</sup> 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<sup>2</sup> 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,<sup>3</sup> it was shown that reactions of this type in the benzoyl carbinol series lend themselves admirably to this kind of treatment.

Zincke<sup>4</sup> 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,<sup>5</sup> 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 alkalis,<sup>6</sup> and copper salts,<sup>7</sup> 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.<sup>8</sup>

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



<sup>1</sup> Ann. Chem., 318, 137; 335, 191; 357, 214.

<sup>2</sup> Am. Chem. J., 38, 561.

<sup>3</sup> Evans, *Ibid.*, 35, 115.

<sup>4</sup> Ber., 13, 635; Ann. Chem., 216, 311.

<sup>5</sup> *Loc. cit.*

<sup>6</sup> Pechmann, Ber., 20, 2904; 22, 2556.

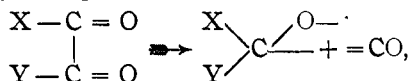
<sup>7</sup> Evans, Am. Chem. J., 35, 124.

<sup>8</sup> *Ibid.*, 38, 584, 585.

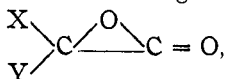
by the addition of one molecule of water, undergo a benzilic acid rearrangement, giving an  $\alpha$ -hydroxy acid,



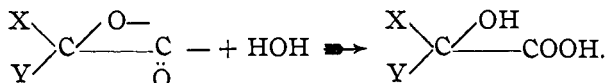
In some cases, such as diketosuccinic ester, hexaketomethylene and diketobutyric ester,<sup>1</sup> this transformation takes place in the presence of water, but in most instances the presence of an alkali is necessary. For this remarkable rearrangement Nef<sup>2</sup> has offered the following explanation: The orthodicarbonyl compound undergoes the following dissociation:



these products of dissociation then uniting to form an  $\alpha$ -lactone,



which then, with a molecule of water, undergoes hydrolysis, forming the corresponding  $\alpha$ -hydroxy acid, as:



The interpretation of Gabriel<sup>3</sup> concerning the transformation of *o*-carboxylbenzoyl-formaldehyde into phthalidcarbonic acid through the intermediate formation of *o*-carboxylmandelic acid becomes, therefore, perfectly evident. Upon this basis, also, the behavior of benzoyl formaldehyde,  $C_6H_5=X$ ,  $H=Y$ ,<sup>4</sup> towards oxidizing agents was readily explained. With mercuric oxide and silver oxide the reactions merely progress through the first stage, the rate of oxidation of the dissociated particles being greater than that of recombination. With copper hydroxide and potassium ferricyanide, in the presence of alkalis, the reaction progressed through the second stage, mandelic acid being the product in each case. The presence of benzoylformic acid in the oxidation with alkaline potassium permanganate is due to the subsequent oxidation of the mandelic acid formed in the second stage, as has been shown by precise experimental data.

Further experiments have been undertaken in this laboratory having for their main purpose: (1) to ascertain whether the same general course of reaction is followed in the substituted benzoyl carbinols as has been developed previously, and (2) to discover what possible effect, if any, the introduction of substituents into the ring might have on these substances towards the oxidizing agents previously considered. This paper, which constitutes a first report on this work, deals solely with the oxidation of

<sup>1</sup> Denis, Am. Chem. J., 38, 590.

<sup>2</sup> Ann. Chem., 335, 272, 273.

<sup>3</sup> Ber., 40, 81, 82.

<sup>4</sup> Loc. cit.

*m*-nitrobenzoylcarbinol. Briefly, the results are as follows: (1) *m*-Nitrobenzoylcarbinol with freshly precipitated mercuric oxide, freshly precipitated silver oxide, and potassium permanganate alone, or in the presence of caustic alkalis, gives *m*-nitrobenzoic acid and carbon dioxide exclusively; (2) *m*-nitrobenzoylcarbinol, with cupric hydroxide and caustic alkalis, gives only *m*-nitromandelic acid; (3) *m*-nitrobenzoylcarbinol, with potassium ferricyanide and potassium hydroxide, gives both *m*-nitrobenzoic acid and *m*-nitromandelic acid. By comparison, it is seen that the differences thus far developed lie in the behavior of *m*-nitrobenzoyl carbinol towards potassium permanganate and alkalis, and potassium ferricyanide and alkalis. The general method previously employed for the preparation of benzoyl carbinol was found to be the most convenient for the preparation of *m*-nitrobenzoyl carbinol, *viz.*, the hydrolysis of the corresponding acetate which had, in turn, been prepared from the bromide.

#### Experimental Part.

*Preparation of m-Nitromonobromacetophenone.*—The following method for the preparation of *m*-nitromonobromacetophenone was found to be much more satisfactory than methods previously described in the literature.<sup>1</sup> A solution of 24.2 grams (one molecule) of bromine in 40 cc. of chloroform was allowed to flow slowly into a warm solution of 25 grams (one molecule) of *m*-nitroacetophenone dissolved in 200 cc. of the same solvent, the operation being carried on in the sunlight. The first red color of the successively added portions of the bromine solution was immediately discharged, the final color of the reaction mixture being yellow. After distilling the chloroform, taking up the residue in ether and washing with dilute sodium carbonate solution, the dried ethereal solution gave a light yellow, crystalline residue, which was identical in every respect with *m*-nitromonobromacetophenone described by Korten and Scholl.<sup>2</sup> This method gave a theoretical yield of 37 grams, which, when purified from a mixture of equal portions of ether and ligroin (60°–80°), gave a melting-point of 96°. The same general procedure may also be followed in the preparation of *m*-nitrodibromacetophenone. Into a boiling solution of 5 grams (one molecule) of *m*-nitroacetophenone, in chloroform, were added slowly 9.69 grams (two molecules) of bromine dissolved in 25 cc. of the same solvent, the operation being carried on in the direct sunlight. The quickly decolorized reaction mixture was then treated as above, giving finally a yield of 9.8 grams of a yellow oil, which solidified on cooling to light yellow crystals melting at 61°<sup>3</sup> (Engler found 59°). Applying the above general method to the preparation of dibromacetophenone, 20 grams (one molecule) of monobromacetophenone, prepared according to the direction of Möhlau,<sup>4</sup>

<sup>1</sup> Hunnius, Ber., 10, 2008. Korten and Scholl: *Ibid.*, 34, 1909.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Ber., 18, 2240.

were dissolved in 100 cc. of boiling chloroform and to this solution were added slowly 16 grams (one molecule) of bromine in 30 cc. of the same solvent. A final yield of 27.0 grams (theory = 27.9 grams) of the crude substance was thus obtained.

*Preparation of m-Nitroacetophenone Acetate.*—In preparing the  $\omega$ -acetate of *m*-nitroacetophenone the same general method was followed as previously indicated by one of us in the preparation of the  $\omega$ -acetate of acetophenone. It was found in the experiment herewith described that the temperature had to be carefully controlled owing to the tendency of the reacting substances to form tar. A mixture of 15 grams (one molecule) of *m*-nitrobromacetophenone, dissolved in 60 cc. of glacial acetic acid, and 7.56 grams (1.5 molecules) of powdered fused sodium acetate, was heated under a reverse condenser on an oil bath, the temperature being brought gradually to 105°, at which point it was maintained for two hours. Sodium bromide began to separate out at 90–95°, the larger portion coming down, however, at 105°. Finally the temperature was raised to 115° for one hour, after which the reaction mixture was poured into six volumes of water. The separated reddish-brown oil soon solidified on standing, after which the crystals were filtered and dissolved in ether. To this solution of the acetate was added that which was obtained by extracting the filtrate six times with ether. The combined solutions were washed with dilute sodium carbonate, after which the dried ether was evaporated to one-fifth of its volume, whereby the acetate began to crystallize out. By successive evaporation of the mother-liquor, a yield of 13.3 grams (theory = 13.7 grams) of the *m*-nitroacetophenone acetate was finally obtained. The substance (m. p. 51°), purified from a mixture of ether and ligroin, gave the following analysis:

Calculated for  $C_{10}H_9O_5N$ : C, 53.81; H, 4.03; N, 6.30. Found: C, 53.89, 53.80; H, 4.10, 4.10; N, 6.70.

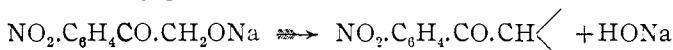
*Preparation of Meta-Nitrobenzoylcarbinol.*—Twenty-five grams of *m*-nitroacetophenone acetate were hydrolyzed by means of 500 cc. of boiling water containing 1 cc. of dilute (1:1) sulphuric acid, the time of hydrolysis being thus reduced from nine to four hours without apparently increasing the yield of tar. After filtering and cooling, 16 grams (theory 20.5 grams) of the light yellow crystalline carbinol were obtained (m. p. 92.5–93°), this yield comprising the product also obtained by the evaporation of the second filtrate to one-fourth of its volume under diminished pressure. The aqueous solution of the carbinol reduces ammoniacal silver nitrate and Fehling's solutions. The analysis of the substance, purified from benzene, was as follows:

Calculated for  $C_8H_7O_4N$ : C, 53.03; H, 3.86; N, 7.73. Found: C, 53.20, 52.97; H, 3.88, 3.83; N, 8.50.

The following special experiment was performed: 0.20 gram of *m*-nitro-

benzoylcarbinol, dissolved in 1 cc. of glacial acetic acid, was acted on by 0.5 cc. of acetyl chloride for one hour at 50°. The oil, obtained by pouring the reaction mixture into 25 cc. of water, soon crystallized and gave 0.18 gram of a product which when purified from ether-ligroin was found to be identical with the acetate above described.

*m*-Nitrobenzoyl Carbinol, Cupric Hydroxide and Sodium Hydroxide.—*m*-Nitrobenzoyl carbinol, like benzoyl carbinol and acetol, reduces Fehling's solution in the cold and also like these two latter substances, gives with alkaline cupric hydroxide the corresponding  $\alpha$ -hydroxy acid, *viz.*, *m*-nitromandelic acid. The point of dissociation of the salts of primary and secondary alcohols being much lower than the free alcohols,<sup>1</sup> this reaction undoubtedly proceeds as follows:



the *m*-nitrobenzoylmethylene thus formed is then oxidized to *m*-nitrobenzoylformaldehyde, which in turn, in the presence of the alkali, undergoes a benzilic acid rearrangement to *m*-nitromandelic acid.<sup>2</sup> The similarity of behavior of *m*-nitrobenzoyl carbinol to acetol and benzoyl carbinol is shown by the following experiment: To a solution of 2.0 grams (one molecule) of *m*-nitrobenzoyl carbinol in 300 cc. of water were added 5.5 grams (two molecules) of crystalline copper sulphate in 20 cc. of water. On the addition to the mixture of 3.31 grams (7.5 molecules) of sodium hydroxide dissolved in 20 cc. of water, an instantaneous reduction to cuprous oxide took place in the cold. After standing 24 hours the yellow oxide was filtered and washed till the total volume was 800 cc. Acidifying with dilute sulphuric acid (1:1) and extracting 6 times with ether a yield of 1.93 grams of *m*-nitromandelic acid was obtained (theory 2.18 grams). A study of the action of copper salts on *m*-nitrobenzoyl carbinol is now being made in this laboratory in the hope of obtaining the intermediate aldehyde. In preliminary experiments with cupric sulphate 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.

*m*-Nitrobenzoyl Carbinol and Potassium Permanganate.—The striking difference in the behavior of benzoyl carbinol and *m*-nitrobenzoyl carbinol towards potassium permanganate and alkalis is shown in the following experiment in which the substituted carbinol gave the corresponding benzoic acid exclusively and no trace of the keto-acid as does the non-substituted substance. A mixture of 2.62 grams (three molecules) of potassium permanganate and 0.66 gram (three molecules) of sodium hydroxide in 100 cc. of water was added to a solution of 1 gram of *m*-nitro-

<sup>1</sup> Nef, Ann. Chem., 318, 138.

<sup>2</sup> Compare Evans, Am. Chem. J., 35, 125. Also Denis, *Ibid.*, 38, 584.

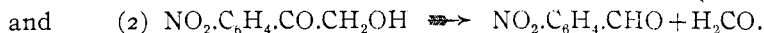
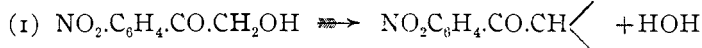
benzoyl carbinol in 150 cc. of water, the resulting temperature being 28°. The color of the first additions of the permanganate was instantly discharged, the reaction being accompanied by a gradual separation of the oxide of manganese. After standing four hours, the excess of permanganate was reduced with a few drops of alcohol, after which the aqueous filtrate was worked up in the usual manner. There was obtained 0.86 gram of the pure *m*-nitrobenzoic acid (theory=0.92 gram). A solution of 5.22 grams of potassium permanganate in 100 cc. of water when added to a solution of 2 grams of *m*-nitrobenzoyl carbinol in 300 cc. of water, reacted instantly when carried out as in the previous experiment, a final yield of 1.78 grams (theory=1.84 grams) of pure *m*-nitrobenzoic acid being obtained—a result in harmony with the studies on benzoyl carbinol. *r*-Lactic acid and *r*-mandelic acid are alike in their general behavior towards alkaline potassium permanganate in that both give acetylformic acid and benzoylformic acid, respectively.<sup>1</sup> In striking contrast to this general behavior is that of *m*-nitromandelic acid, which with these agents gives *m*-nitrobenzoic acid exclusively as is proved by the following experiment: A mixture of 2 grams of *m*-nitromandelic acid and 0.84 gram of potassium hydroxide in 50 cc. of water was added to a solution of 3.20 grams (two molecules) of potassium permanganate and 1.12 grams (two molecules) of potassium hydroxide in 100 cc. of water. After standing twenty-four hours, a yield of 1.61 grams (95 per cent. of theory) of pure *m*-nitrobenzoic acid was obtained. From this behavior of *m*-nitromandelic acid towards alkaline potassium permanganate, it was concluded that *m*-nitrobenzoylformic acid should also be completely oxidized to *m*-nitrobenzoic acid. That this expectation was fully realized is shown by the following experiment: To a solution of 4.03 grams (one molecule) of *m*-nitrobenzoylformic acid and 1.03 grams (1.25 molecules) of sodium hydroxide in 100 cc. of water was added a solution of 3.45 grams of potassium permanganate in 100 cc. of water. After standing at room temperature for twenty-four hours the reaction mixture yielded 3.29 grams (theory=3.45 grams) of *m*-nitrobenzoic acid.

*m*-Nitrobenzoyl Carbinol, Potassium Ferricyanide and Potassium Hydroxide.—*m*-Nitrobenzoyl carbinol in its behavior towards alkaline potassium ferricyanide is different from benzoyl carbinol in that it gives *m*-nitrobenzoic acid in addition to its corresponding hydroxy acid, as the following experiment shows: One gram of *m*-nitrobenzoyl carbinol dissolved in 150 cc. of water was added to a mixture of 10.91 grams (six molecules) of potassium ferricyanide and 2.48 grams (eight molecules) of potassium hydroxide dissolved in 100 cc. of water, the resulting temperature being 28.5°. After standing over night the solution was acidified with dilute

<sup>1</sup> Compare Ulzer and Seidel, *Monatsh. Chem.*, 18, 138. Also Denis, *Am. Chem. J.*, 38, 575.

sulphuric acid and extracted six times with ether. There was thus obtained 0.93 gram of acid material (m. p. 85-95°) which, upon dissolving in 15 cc. of hot water and cooling suddenly, gave 0.27 gram of a flaky precipitate (m. p. 138-139°) which proved to be *m*-nitrobenzoic acid, the aqueous filtrate containing *m*-nitromandelic acid. A study of the behavior of *m*-nitromandelic acid towards alkaline potassium ferricyanide was made as follows: To a solution of 2.0 grams (one molecule) of *m*-nitromandelic acid and 3.98 grams of potassium hydroxide (seven molecules) in 50 cc. of water were added 16.71 grams of potassium ferricyanide, the resulting temperature being 24°. After standing twenty-four hours and working up as above a yield of 1.75 grams (m. p. 85-90°) of acid material was obtained which gave no reaction with phenylhydrazine<sup>1</sup> thus showing the absence of *m*-nitrobenzoylformic acid. In view of this result, the following experiment needs no further explanation: To a solution of 1.33 grams (one molecule) of *m*-nitrobenzoylformic acid and 1.00 gram of sodium hydroxide, in 100 cc. of water, were added 13.47 grams of potassium ferricyanide and 2.26 grams of potassium hydroxide in 100 cc. of water. After standing at room temperature for 24 hours, the reaction mixture yielded 1.10 grams (theory = 1.14 grams) of *m*-nitrobenzoic acid. The reaction mixtures when acidified with dilute sulphuric acid gave the Prussian blue test with ferric chloride.

*m*-Nitrobenzoyl Carbinol and Silver Oxide.—*m*-Nitrobenzoyl carbinol when acted upon by silver oxide either in the presence or absence of alkalis gives *m*-nitrobenzoic acid, a result which is in harmony with the action of the same reagents on benzoylcarbinol and with the experiments of Denis on acetol.<sup>2</sup> It is perfectly evident that *m*-nitrobenzoyl carbinol possesses a possibility of dissociating in two directions, viz.:



Consequently, in the absence of alkalis, it is possible for *m*-nitrobenzoic acid to arise from an oxidation of the dissociated particles in equation (2).<sup>3</sup> One gram (one molecule) of *m*-nitrobenzoyl carbinol dissolved in 150 cc. of water was added to 2.5 molecules of freshly precipitated and well washed silver oxide, prepared from 4.68 grams of silver nitrate. On standing nine hours at room temperature a slight reduction was observed, accompanied by a brown coloration of the carbinol solution. The temperature was raised to 70° for one hour and finally to 100° till the evolution of carbon dioxide ceased, determined by its action on barium

<sup>1</sup> Fehrlin, Ber., 23, 1576.

<sup>2</sup> Am. Chem. J., 38, 579.

<sup>3</sup> Compare Evans, Am. Chem. J., 35, 129. Nef, Ann. Chem., 335, 269. Also Kling, Ann. chim. phys. (8), 5, 529.

hydroxide solution. Treating the reaction mixture with an excess of ammonium hydroxide, carefully acidifying the filtrate from the metallic silver and working up in the usual way, there was obtained 0.80 gram (theory = 0.92) of *m*-nitrobenzoic acid. The action of *m*-nitrobenzoyl carbinol on silver oxide in the presence of alkalis was carried on as follows. A solution of 1 gram of the carbinol in 150 cc. of water was added slowly to four molecules of freshly precipitated and well washed silver oxide (from 4.68 grams of silver nitrate) suspended in 50 cc. of an aqueous solution of sodium hydroxide containing 1.13 grams, the resulting temperature being 29°. At the end of three days the reaction mixture gave 0.74 gram (80 per cent.) of *m*-nitrobenzoic acid and 2.19 grams (theory = 2.56 grams) of metallic silver. The following special experiment shows that the presence of *m*-nitrobenzoic acid could not be attributed to the intermediate formation of *m*-nitromandelic acid and its subsequent oxidation. Two grams of *m*-nitromandelic acid and 0.85 gram sodium hydroxide dissolved in 100 cc. of water were added to an emulsion of 4.71 grams of freshly precipitated and well washed silver oxide, prepared from 6.94 grams of silver nitrate. After standing at room temperature for 24 hours and working up the reaction mixture in the usual way, 1.90 grams of the original acid were recovered. A similar result was obtained by allowing the reaction mixture to stand six weeks.

*m*-Nitrobenzoyl Carbinol and Mercuric Oxide.—The recent experiments of Denis<sup>1</sup> confirm the observations of Nef and Kling; namely, that acetyl with mercuric oxide in the presence of alkalis gives *r*-lactic acid instead of acetic acid, as one would expect from the course of the analogous reaction in the aromatic series. *m*-Nitrobenzoyl carbinol is analogous to the behavior of benzoyl carbinol towards alkaline mercuric oxide as the following experiments show: A solution of 1 gram of *m*-nitrobenzoyl carbinol in 150 cc. of water was added to 2.5 molecules of freshly precipitated and well washed mercuric oxide (from 3.74 grams of mercuric chloride) and 1.54 grams of sodium hydroxide, reduction taking place instantly. After standing 24 hours the reaction mixture yielded 0.68 gram of *m*-nitrobenzoic acid. Repeating the same experiment but in the absence of alkali, there was obtained 0.84 gram of *m*-nitrobenzoic acid. In the latter experiment, however, the reaction mixture after standing 24 hours was kept on a boiling water bath for six hours, during which time a large amount of barium carbonate was precipitated from the attached barium hydroxide solution. A special experiment with *m*-nitromandelic acid and alkaline mercuric oxide showed that this substance is similar in its behavior towards these agents as it is towards silver oxide and caustic alkalis. One gram (one molecule) of *m*-nitromandelic acid and 1.10 grams of sodium hydroxide dissolved in 100 cc. of water, when

<sup>1</sup> *Loc. cit.*



added to 2.73 grams of freshly precipitated and well washed mercuric oxide (from 3.43 grams of mercuric chloride), gave no evidence of any reduction having taken place at the end of 24 hours. After working up in the usual way 0.92 gram of the unchanged acid was recovered.

### LONG LEAF PINE OIL.

By J. E. TEEPLE.

Received January 2, 1908.

Long leaf pine oil, as its name indicates, is an oil derived from the *pinus palustris* or long leaf pine. Specifically, it is that particular pine oil which is obtained as a by-product in the extraction of turpentine from lightwood by means of steam. It merits our consideration here first because it is a new product commercially; second because of the great variety of uses which have been found for it; and third because its uniformity and the large quantities in which it can be furnished indicate that it will probably become a permanent source of valuable terpene derivatives.

The statements regarding long leaf pine oil given here refer only to the product made by steam distillation.<sup>1</sup> The rosin bath process and the destructive distillation systems, of course, give fractions of oil having more or less similar properties, but in the one case they are contaminated with products of rosin distillation and in the other case with creosote-like compounds.

Three years ago the sale of long leaf pine oil was almost negligible, and the greater portions of those fractions of the distillate which contained the oil were thrown away without purification. To-day the product is sold regularly in carload lots. As to its uses it has been found that it will dissolve any of the ordinary varnish gums cold, whereas in the usual methods of manufacturing varnishes the gums must be melted before they dissolve properly. This same solvent power makes it valuable in varnish works for washing filter cloths. It is likewise one of the best solvents for rubber. It can be added to a lacquer made from nitrocellulose dissolved in amyl acetate without precipitating the nitrocellulose. It is not of itself a rapid hard drying oil and so is often used in the coating of insulated cables. The high price of oil of camphor and the more stringent laws regarding the use of benzine have led to the substitution of pine oil almost exclusively for these two products in the manufacture of metal polishes. When properly refined it has a very pleasant odor which leads to its use by the essential oil trade in general and by soap makers in particular for perfuming cheaper soaps.

Regarding the composition of the long leaf pine oil, it has been generally

<sup>1</sup> J. S. C. I., 26, 811.