dride. The solution is warmed slightly and allowed to stand for twenty-four hours. It is then evaporated to dryness under reduced pressure and the residue extracted with ether. The ether is removed, the crude material dissolved in chloroform and precipitated by the addition of petroleum ether.

The acetamino compound can be more conveniently prepared from the triacetate by partial hydrolysis according to a method devised by Kehrmann and Hoehn.[8] The triacetate is added to 33% sodium hydroxide solution, and goes into solution with evolution of heat. In a few minutes the acetyl groups are hydrolyzed, after which the solution is cooled to 0° and neutralized with sulfuric acid. The acetamino compound is extracted with ether and purified as before. The yield is not good by either method of preparation. It is easily soluble in water, but slightly soluble in the hot solutions. It is insoluble in petroleum ether. From toluene or chloroform it forms white microscopic blades, melting at 124–125°. From water it forms regular tetrahedra, but crystallization is attended by gum formation. The 3-acetaminopyrocatechol forms a gray lead salt and gives an olive green color with ferric chloride. In contact with the air the aqueous solution assumes a red color which is probably due to quinone formation, since the color is discharged by sulfur dioxide.

*Anal.* (Kjeldahl). Subs., 0.2074: 5.96 cc. of 0.2035 $N$ HCl. Calcd. for $C_8H_9O_3N$: N, 8.38. Found: 8.21.

The isomeric 4-acetaminopyrocatechol was prepared intermediately by Kehrmann and Hoehn but not isolated.

## Summary

Pyrocatechol has been nitrated and the process for the separation of the isomers definitely established. The corresponding amines have been prepared by direct reduction, and 3-aminopyrocatechol and some compounds arising from it have been described. The procedure for the preparation of other pyrocatechols substituted in either the 3- or 4-position has thus been simplified. Further work along this line is in progress in this Laboratory.

UNIVERSITY, MISSISSIPPI

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 616]

# THE CHEMISTRY OF THE ACYL PARA-QUINONES. A CONTRIBUTION TO THE SOLUTION OF THE "PECHMANN DYES" PROBLEM[1]

BY MARSTON TAYLOR BOGERT AND HENRY PRICE HOWELLS[2]

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By the action of acetic anhydride upon $\beta$-benzoylacrylic acid, and some of its homologs, von Pechmann[3] obtained, in 1882, deeply colored products whose chemical constitution he did not ascertain. These products, which have been known since as "Pechmann Dyes," were studied twenty-four years later by Kozniewski and Marchlewski,[4] who assigned to them the

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[1] Presented in abstract before the Division of Organic Chemistry, at the St. Louis Meeting of the American Chemical Society, April, 1928.

[2] Recently Lydia C. Roberts Graduate Fellow at Columbia University.

[3] Von Pechmann, *Ber.*, **15**, 885 (1882).

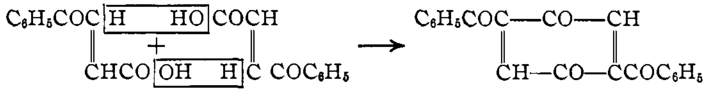
[4] Kozniewski and Marchlewski, *Bull. acad. sci. Cracow,* 81 (1906).

structures of diaroyl *p*-quinones. In 1924 Bogert and Ritter[5] attacked the problem and, as the result of their experimental work, came to the conclusion that these compounds did not possess the constitution ascribed to them by Kozniewski and Marchlewski, but that the simplest Pechmann Dye at least was probably the *trans*-dilactone of diphenacylmaleic acid.

Although the evidence upon which this conclusion was based seemed good, it was decided to follow the matter further by the study of diaroyl *p*-quinones prepared in other ways. These syntheses and studies are recorded in the following pages, and support the contention that the Pechmann Dyes do not belong to this class.

At the time this research was begun, aside from the Pechmann Dyes, we were unable to find any mention of acylated *p*-quinones in the literature, and there was therefore the added incentive of contributing something to fill this gap.

Kozniewski and Marchlewski explained the formation of the simplest Pechmann Dye thus



$$\begin{array}{l} C_6H_5COC\boxed{H \quad HO}COCH \\ \quad\| \qquad + \qquad \| \\ CHCO\boxed{OH \quad H}C\ COC_6H_5 \end{array} \longrightarrow \begin{array}{l} C_6H_5COC—CO—CH \\ \qquad\quad \| \qquad\quad \| \\ \qquad\ CH—CO—CCOC_6H_5 \end{array}$$

The crux of the problem was, therefore, the synthesis of 2,5-dibenzoyl-*p*-benzoquinone by some other method and the determination of its identity or non-identity with this Pechmann Dye. The steps in this synthesis are shown on the Flow Diagram herewith and although we have not succeeded in proving conclusively that the two benzoyl groups are in the para position to each other, the evidence is all in favor of such an assumption. We have at least demonstrated that the dibenzoylbenzoquinone synthesized in this way exhibits properties which are quite different from those of the Pechmann Dye.

Since the simplest method of preparing such acylated quinones was obviously the oxidation of the corresponding acylated hydroquinones, it became necessary to develop improved methods for the synthesis of these latter, for the methods already in the literature were not very satisfactory.

The acylation of dihydric phenols has been studied more frequently and more successfully in the case of resorcinol than with either of its isomers. Methods which proved satisfactory when applied to resorcinol have given either much reduced yields or no yields at all when applied to hydroquinone, due largely to the much greater sensitivity and reactivity of this isomer.

The monobenzoylhydroquinone was obtained in good yields by starting with the dimethyl ether of hydroquinone, introducing the benzoyl group by a Friedel–Crafts reaction and demethylating in two steps.

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[5] Bogert and Ritter, (a) THIS JOURNAL, **46**, 2871 (1924); (b) *Proc. Nat. Acad. Sci.*, **10**, 363 (1924).

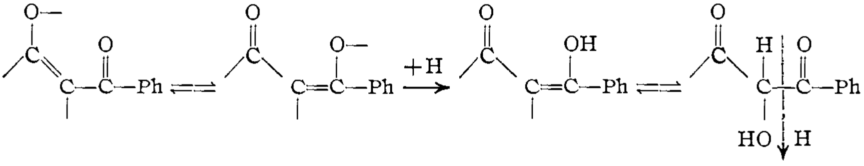
Dibenzoylhydroquinone was secured from hydroquinone dibenzoate, benzoyl chloride and anhydrous aluminum chloride, at temperatures near 200°, by a modification of the process of Doebner and Wolff.[6] The failure of the experiments designed to establish the location of the benzoyl groups was due in part to the difficulty encountered in reducing the benzoyl groups to the corresponding hydrols, and in part to our inability to obtain a pure dibromo substitution product of the diacylated hydroquinone.

Both mono- and dibenzoylhydroquinones were oxidized smoothly to the corresponding acylated quinones by cold chromic acid mixture.

It has been shown that a benzoyl group adjacent to a methoxyl renders the latter much less stable to demethylating agents. Thus the partial demethylation of monobenzoylhydroquinone dimethyl ether, as carried out by Kauffmann and Grombach,[7] was shown by Auwers and Rietz[8] to be the 2-hydroxy-5-methoxybenzophenone, with which conclusion Kauffmann agreed, in a private communication,[8] after showing that one of the methoxyl groups in nitrohydroquinone was more readily demethylated than the other. Our own results are in harmony with these, for both of the methyl groups were easily removed from dibenzoyl hydroquinone dimethyl ether, and this is therefore an additional support of the assumption that the two benzoyl groups were not adjacent to the same methoxyl in our product.

Comparative oxidation and reduction reactions carried out with these benzoylated hydroquinones and quinones showed quite clearly that the monobenzoylhydroquinone was more rapidly oxidized, in either acid or alkaline solution than the dibenzoyl and that, as might have been expected, the dibenzoyl quinone was the more rapidly reduced. Similarly, the dibenzoylhydroxyhydroquinone was less rapidly oxidized than the monobenzoyl.

In the attempted reduction of dibenzoylhydroquinone to the dihydrol by the action of 3% sodium amalgam upon its suspension in water, a strong odor of benzaldehyde was soon apparent. The blood-red color which always developed when the yellow crystals of either the mono- or dibenzoylhydroquinone were dissolved in caustic alkali, suggests a tautomeric change, analogous to that occurring in the case of $\beta$-diketones, which perhaps may be formulated thus



(A) yellow (B) blood-red (C) (D)

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[6] Doebner and Wolff, *Ber.*, **12**, 661 (1879).

[7] Kauffmann and Grombach, *Ann.*, **344**, 30 (1906).

[8] Auwers and Rietz, *Ber.*, **40**, 3514 (1907).

It is suggested that the quinoid structure (B) represents the blood-red form, whose reduction should lead to (C) and (D), hydrolysis of which by the alkali should yield benzaldehyde.

The Pechmann Dye yields benzoic acid when oxidized by hot chromic acid mixture or alkaline permanganate; the dibenzoyl quinone described herein gives the same acid when oxidized cold by these reagents.

In glacial acetic acid solution both benzoyl quinones reacted instantly with aniline to form beautifully crystalline precipitates. That from the monobenzoyl derivative was deep purplish red and proved to be the dianilino-monobenzoylquinone. That from the dibenzoyl quinone was a monoanilino-dibenzoylhydroquinone and was bright yellow. Under similar conditions the Pechmann Dye condenses immediately with two moles of aniline to a dark green crystalline product which Kozniewski and Marchlewski[4] believed to be the dianilide of dibenzoyl quinone, but which the recent work of Bogert and Greenberg[9] has shown to be most probably the N,N′-diphenyl dilactam of diphenacylfumaric acid. In the case of both quinones the aniline appeared to act preferably upon the hydrogens of the nucleus, to form aniline derivatives, the dibenzoyl derivative, presumably because of its greater affinity for hydrogen, being reduced to the hydroquinone, whereas the monobenzoyl compound remained as the quinone; or, there may have occurred addition in both instances, followed by oxidation in the case of the monobenzoyl product and reduction in that of the dibenzoyl.

The latter hypothesis appears the more plausible in the light of the behavior of the two quinones with acetic anhydride containing a trace of concentrated sulfuric acid, following the method used by Thiele[10] for studying 1,4-addition to unsaturated $\gamma$-diketone types. Both quinones yielded the corresponding mono- and di-benzoylhydroxyhydroquinone triacetates, from which the hydroxyhydroquinones themselves were easily secured. So far as we are aware, this is the only method as yet described for the preparation of these diacylated trihydric phenols.

Inasmuch as in the formation of the Pechmann Dye from acetic anhydride and benzoylacrylic acid considerable amounts of unidentified by-products are separated, it seemed possible, were this dye actually a dibenzoylquinone, that some of these by-products might have been formed by addition reactions similar to the above, but a careful examination of them showed that they were not.

## Experimental

**1,4-Dimethoxybenzene.**—The method used by Ullmann[11] for the preparation of this compound was modified as follows. To a solution of 50 g. of hydroquinone in 275

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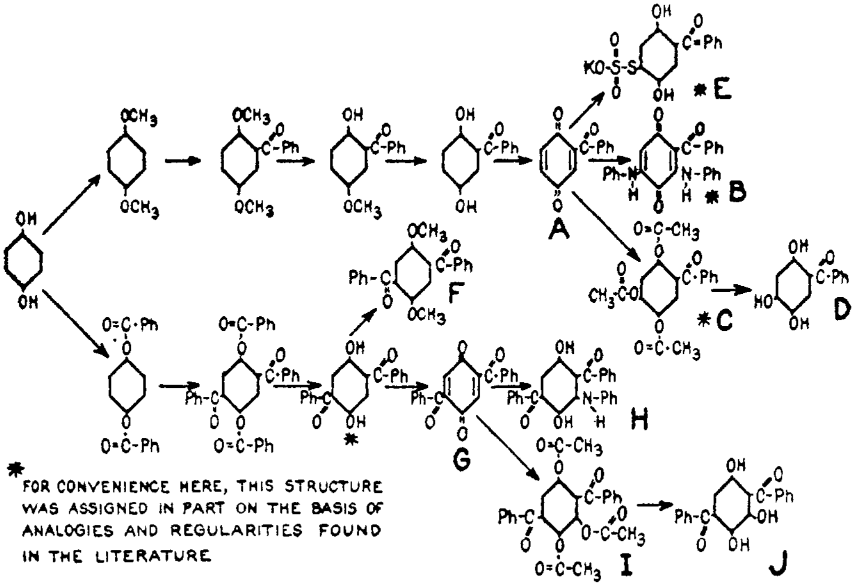
[9] Bogert and Greenberg, unpublished results. See "Dissertation" by Irving W. Greenberg, Columbia University, **1926**.

[10] Thiele, *Ber.*, **31**, 1247 (1898).

[11] Ullmann, *Ann.*, **327**, 104 (1903).

cc. of 15% sodium hydroxide there was added slowly and with vigorous shaking 105 cc. of methyl sulfate, allowing the temperature to rise gradually to 50° until most of the methyl sulfate had been added, then interrupting its addition for a short time while continuing the shaking, finally running in the remainder and renewing the agitation for a further ten minutes. Excess of methyl sulfate was destroyed by addition of 50 cc. of 10% sodium hydroxide and heating for an hour at 100°. As the solution cooled, the dimethyl ether crystallized. It was collected, washed, dried and crystallized from 75% alcohol, when it appeared in large colorless lustrous flakes, of strong but agreeable ethereal odor, m. p. 56.8° (corr.); yield, 55.5 g., or 88.5%. Ullmann reported the m. p. as 56°.



*FOR CONVENIENCE HERE, THIS STRUCTURE WAS ASSIGNED IN PART ON THE BASIS OF ANALOGIES AND REGULARITIES FOUND IN THE LITERATURE.

Flow sheet.

Monobenzoylhydroquinone dimethyl ether (2,5-dimethoxybenzophenone), $C_6H_5$-$COC_6H_3(OCH_3)_2$, was prepared from hydroquinone dimethyl ether, benzoyl chloride and anhydrous aluminum chloride, in carbon disulfide solution, according to the process of Kauffmann and Grombach.[7] The crude product was freed from unaltered initial material and from the monomethyl ether (formed as a by-product to the extent of about 10%) by long continued and repeated steam distillation of a strongly alkaline solution. Crystallized from methyl alcohol, the benzoylated dimethyl ether was obtained in colorless crystals, m. p. 51.2° (corr.); yield, about 40%. Kauffman and Grombach reported a melting point of 51° for yellow crystals, Herzig and Hofmann[12] a melting point of 50–52° for colorless ones.

When this dimethyl ether was heated with constant-boiling hydrobromic acid for two and one-half hours at 130–140° in sealed tubes, hydrolysis apparently occurred, for the only product identified was benzoic acid.

Monobenzoylhydroquinone Monomethyl Ether (2-Hydroxy-5-methoxybenzophenone) $C_6H_5COC_6H_3(OH)OCH_3$.—By the following variations in the procedure employed for the synthesis of the dimethyl ether, the monomethyl ether was made the principal instead of the by-product. To a solution of 50 g. of hydroquinone dimethyl

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[12] Herzig and Hofmann, *Ber.*, **41**, 143 (1908).

ether and 50 g. of benzoyl chloride in 50 cc. of carbon disulfide, there was added slowly (one and one-half hrs.) 60 g. of finely pulverized anhydrous aluminum chloride, the temperature of the mixture being kept at about 25°. After standing for forty-eight hours at room temperature, the reaction was completed by warming for thirty minutes at about 50°. The dark resinous mass was hydrolyzed with cracked ice and concentrated hydrochloric acid and the yellow product distilled with steam for two hours to free it from carbon disulfide and most of the unaltered initial hydroquinone dimethyl ether. The brown oil remaining was dissolved in ether, the ethereal solution dried with calcium chloride, the solvent evaporated, the brown oily residue dissolved in 75 cc. of dry benzene, and to this solution 35 g. of finely pulverized anhydrous aluminum chloride was added at such a rate as to maintain a brisk evolution of hydrogen chloride. After all of the aluminum chloride had been added, the temperature of the mixture was raised gradually to the boiling point and gentle refluxing continued until hydrogen chloride was no longer evolved. A deep red solution resulted which was cooled and decomposed by 6 *N* hydrochloric acid. Steam distillation removed the benzene and toluene (formed in the reaction), leaving a brown oil which changed to a yellowish solid as it cooled. This crude product was washed with water, dried, dissolved in a large volume of 70–75% alcohol and the solution allowed to cool slowly to room temperature.

A very impure product separated as a heavy dark oil and 30 g. of fairly pure material was recovered by chilling the decanted supernatant liquid. The impure heavy dark oily portion was dissolved in 10% sodium hydroxide with some difficulty, the alkali solution washed with ether and then acidified to faint turbidity. Precipitation was completed by saturating the solution with carbon dioxide. The precipitate was removed, washed with water and crystallized from 80% alcohol, giving 20.5 g. of bright yellow plates, m. p. 84–85.5° (corr.); total yield, 50.5 g., or 55%. Kauffmann and Grombach[7] gave the melting point as 78°, Herzig and Hofmann[12] as 82–85°. Both groups of investigators obtained their product by the action of hydriodic acid upon the dimethyl ether.

A solution of 0.1 mole of monobenzoylhydroquinone dimethyl ether in 10 cc. of carbon disulfide was treated with an equimolar quantity of benzoyl chloride and anhydrous aluminum chloride, the mixture allowed to stand for twenty-four hours, then heated for three hours at 50–60° and worked up in the customary manner; the main product isolated was this same monomethyl ether (m. p. 84–85.5°, corr.), and no dibenzoyl derivative was obtained.

When this monomethyl ether was heated at 135–140° in sealed tubes with constant-boiling hydrobromic acid, hydrolysis apparently ensued, for the amount of benzoic acid isolated nearly equaled that calculated.

**Monobenzoylhydroquinone (2,5-Dihydroxybenzophenone),** $C_6H_5CO$-$C_6H_3(OH)_2$.—Klinger[13] has reported the formation of this compound when hydroquinone was heated with an excess of benzoic acid in the presence of anhydrous zinc chloride, following the analogous work of Nencki and Schmid,[14] whose experiments were conducted with aliphatic and not aromatic acids. Klinger stated further that his results with benzoic were much less favorable than with aliphatic acids, and that the principal product isolated was hydroquinone dibenzoate. Our experience with this process was less satisfactory even than Klinger's, for we succeeded in isolating only a trace of monobenzoylhydroquinone, the main product being, as he found, the hydroquinone dibenzoate (mixed m. p., 204°, corr.).

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[13] Klinger, *Ann.*, **382**, 211 (1911).

[14] Nencki and Schmid, *J. prakt. Chem.*, [2] **23**, 546 (1881).

The observation of Klinger and Standke[15] that monobenzoylhydroquinone was formed when a mixture of benzoquinone and benzaldehyde was exposed to the action of direct sunlight for long periods of time could not be utilized as the basis of a practical method of preparation.

Finzi[16] heated hydroquinone, or its dibenzoate, in nitrobenzene solution, with benzoyl chloride in the presence of anhydrous aluminum chloride and reported the formation of the keto derivative. Our repetition of this work, involving also several attempted variations, yielded, aside from the dibenzoate (mixed m. p., 204°, corr.), only dark colored decomposition products. These results are in agreement with those of Perrier,[17] who found that whereas aliphatic acid chlorides, in the presence of aluminum chloride, condensed with mononuclear phenols, in carbon disulfide solution, to keto derivatives, aromatic acid chlorides under the same conditions formed only the phenolic esters.

The Hoesch[18] reaction proved equally unsuccessful. This involved the action of dry hydrogen chloride upon a solution of hydroquinone and benzonitrile in dry ether, in the prrsence of anhydrous zinc chloride. No keto derivative was obtained. The sole product isolated, even when a large excess of the nitrile was present, was hydroquinone monobenzoate (colorless feathery needles; mixed m. p. 164.5° corr.).

Kauffmann and Grombach[7] were unsuccessful in their attempt to demethylate completely the benzoylhydroquinone dimethyl ether by refluxing it with three parts of constant-boiling hydriodic acid, for only one methyl group was removed. Two years later, Herzig and Hofmann[12] accomplished this demethylation by using six parts of hydriodic acid and long continued refluxing. Our own experience with this latter method was decidedly disappointing, both from the standpoint of time consumed (twelve hours) and yields (5%) of pure product.

We found, however, that benzoylhydroquinone monomethyl ether could be satisfactorily demethylated by the following process.

Sixteen parts of the monomethyl ether was refluxed for one and one-half hours with 2.5 parts of constant-boiling hydriodic acid, 20 cc. of glacial acetic acid and 4 cc. of acetic anhydride, and the clear orange solution poured into 100 cc. of cold water. The yellow crystalline precipitate was washed with water, dried and crystallized from benzene, when it formed yellow crystals, m. p. 125–126.1° (corr.); yield, 13 g., or 87%. Herzig and Hofmann gave the melting point as 122–124°; Klinger and Standke[15] as 125°.

Based upon an earlier observation of Weishut,[19] Pregl[20] recommended the addition of a few drops of acetic anhydride or a few crystals of phenol to the hydriodic acid mix-

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[15] Klinger and Standke, *Ber.*, **24**, 1340 (1891).

[16] Finzi, *Monatsh.*, **26**, 1119 (1905).

[17] Perrier, *Compt. rend.*, **116**, 1140 (1893).

[18] Hoesch, *Ber.*, **48**, 1122 (1915).

[19] Weishut, *Monatsh.*, **34**, 1549 (1913).

[20] Pregl, "Quantitative Organic Microanalysis," translated by Fyleman, Philadelphia, P. Blakiston's Son and Co., **1924**, p. 153.

ture when determining quantitatively the methoxyl group in ethers which are difficult to demethylate. The accelerating influence of these additions upon the rate of demethylation has been ascribed to increased solubility effect. In the demethylation of the monomethyl ether as carried out by us, glacial acetic acid was an excellent solvent and worked well alone, but the addition of the acetic anhydride appeared to bring the reaction to completion in less time.

**Monobenzoyl-*p*-benzoquinone,** $C_6H_5COC_6H_3O_2$.—A solution of 10 g. of monobenzoylhydroquinone in 50 cc. of glacial acetic acid was added very slowly (twenty minutes) to a mixture of 8 g. of sodium dichromate, 10 cc. of concentrated sulfuric acid and 350 cc. of water, while the temperature was maintained in the vicinity of 10° and the solution was vigorously stirred. This stirring was continued for about ten minutes after all of the hydroquinone had been added and until the color of the mixture changed to a dark reddish brown. The suspended product was immediately filtered out, washed well with water and dried. It amounted to about 9 g. Recrystallized from 500 cc. of ligroin (b. p. 70–100°), it gave 7.5 g. of orange yellow lustrous flattened needles, m. p. 85–85.6° (corr.); yield, 77%. The chief impurity in the crude product seemed to be a trace of benzoic acid.

The recrystallization from ligroin proved quite troublesome, because of the tendency of the solution to separate a dark brown difficultly soluble precipitate. This was avoided by adding the finely powdered crude product to the boiling solvent with simultaneous mechanical stirring.

*Anal.* Calcd. for $C_{13}H_8O_3$: C, 73.57; H, 3.81. Found: C, 73.47; H, 3.83.

The purified quinone was soluble in most of the usual neutral organic solvents. In hot water it dissolved but slightly, giving a reddish solution, due perhaps to some incipient chemical change. It was attacked by dilute aqueous caustic alkali, with formation of a brownish solution, from which a light brown flocculent precipitate containing some benzoic acid was thrown down on acidification. It was easily reduced by sulfurous acid to the original hydroquinone again. With hydroxylamine, under various conditions, the quinone failed to yield sufficient oxime to be isolated and identified, probably due to the sensitiveness of the quinone to the reducing action of the hydroxylamine.

**Dianilino-monobenzoyl-*p*-benzoquinone,** $C_6H_5CO(C_6H_5NH)_2C_6HO_2$.—A solution of 2 g. of aniline in 4 cc. of glacial acetic acid was added to one of 1.6 g. of monobenzoyl quinone in 20 g. of the same solvent while warm. The mixture turned deep red immediately. After warming for a few minutes longer, it was left for half an hour at room temperature and was then stirred vigorously. A deep purplish red crystalline precipitate separated and the separation was complete at the end of an hour. The precipitate was collected, washed with glacial acetic acid, then with alcohol, dried and recrystallized from a large volume of alcohol. As thus purified, the product formed diamond-shaped plates which appeared red by transmitted and purple by reflected, light, m. p. 211.7–212.2° (corr.). From a small volume of hot benzene clusters of small purplish red plates were obtained, m. p. 212.2–212.7° (corr.); yield, about 1 g., or 34%.

*Anal.* Calcd. for $C_{25}H_{18}O_3N_2$: C, 76.09; H, 4.60. Found: C, 76.17; H, 4.62.

This method of preparation resembles that used by Zincke and Hagen[21] for the preparation of anilino derivatives of *p*-benzoquinone itself, except that with this acyl derivative the formation of dianilino-anilide was not observed.

This dianilino-benzoyl-quinone was unaffected by hot sulfurous acid, and was not acetylated when heated with acetic anhydride and fused sodium acetate, a behavior which has been observed before[22] in the case of such dianilino derivatives. In con-

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[21] Zincke and Hagen, *Ber.*, **18**, 785 (1885).

[22] Fischer and Hepp, *ibid.*, **21**, 683 (1888).

centrated sulfuric acid it dissolved slowly to a deep red solution, but was insoluble in dilute acid or in alkali.

**Monobenzoylhydroxyhydroquinone Triacetate,** $C_6H_5COC_6H_2(OCOCH_3)_3$.—The Thiele[10] method for effecting 1,4-addition to unsaturated γ-diketones was applied to the benzoyl quinone with interesting results.

To 6 g. of acetic anhydride, containing three drops of concentrated sulfuric acid, there was added 2 g. of the benzoyl quinone and the reaction was completed by warming for two to three minutes at 40–50°. The yellow solution gradually lost nearly all of its color. It was poured into cold water and the mixture allowed to stand until the hydrolysis of the excess of acetic anhydride was completed. The colorless precipitate was removed, washed with water, dried and crystallized from alcohol, when it appeared in glistening colorless needles, m. p. 137.7° (corr.); yield, 1.1 g.

*Anal.* Calcd. for $C_{19}H_{16}O_7$: C, 64.03; H, 4.53. Found: C, 63.86; H, 4.53.

In cold 0.5 *N* caustic alkali the compound was insoluble, but when heated it gave a greenish black solution apparently due to hydrolysis and subsequent oxidation. Attempts to convert this triacetate, by the action of methyl sulfate and alkali, into the 2,4,5-trimethoxybenzophenone of Bargellini and Martegiani[23] were unsuccessful.

**Monobenzoylhydroxyhydroquinone,** $C_6H_5COC_6H_2(OH)_3$.—A solution of 2 g. of the above triacetate in 20 cc. of absolute alcohol saturated with dry hydrogen chloride was refluxed for about two hours, the alcohol and ethyl acetate then removed by distillation under diminished pressure and the residual reddish oil shaken with cold water. The yellow crystalline mass thus formed was filtered out, washed with water, dried and crystallized from a mixture of equal parts of benzene and ligroin (b. p. 70–100°). Fine orange yellow crystals were thus obtained, m. p. 129.1° (corr.); yield, 1 g., or 77%.

*Anal.* Calcd. for $C_{13}H_{10}O_4$: C, 67.84; H, 4.38. Found: C, 68.00; H, 4.45.

The compound dissolved in dilute aqueous caustic alkali to a reddish orange solution which changed to a greenish black after a brief exposure to the air. Acidification of the reddish orange solution re-precipitated the original benzoylhydroxyhydroquinone, but this did not occur in the case of the greenish black solution. This hydroquinone stained the skin a rather fast black.

**Monobenzoylhydroquinone Thiosulfuric Acid,** $C_6H_5COC_6H_2(OH)_2SSO_3H$.—Patents were taken out in 1908 by the Badische Anilin und Soda-Fabrik[24] for the production of hydroquinone thiosulfuric acids from *p*-quinones and for their utilization as dye intermediates. Hydroquinone thiosulfuric acid is described therein as being easily condensed with 2-amino-5-dimethylaniline thiosulfuric acid in alkaline solution by means of air oxidation to give a blue violet dye. The specifications of these patents were applied, with minor changes, to the monobenzoyl quinone as follows.

A warm (40–50°) solution of 5 g. of monobenzoylquinone in 28 cc. of glacial acetic acid was run into a solution of 9 g. of sodium thiosulfate in an equal weight of water, while the temperature was maintained within a few degrees of that of the room. After standing for two hours at room temperature, the clear yellow solution had deposited a small amount of benzoylhydroquinone as a fine yellow solid and more was separated by addition of several volumes of water. The mixture was allowed to stand for an hour more, the suspended benzoylhydroquinone filtered out and the filtrate saturated with potassium chloride. The potassium salt of the thiosulfuric acid separated in pale yellow crystals, which were collected, washed with a 5% potassium chloride solution, then with water and finally with alcohol. The dried product (6 g.) was recrystallized from hot

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[23] Bargellini and Martegiani, *Gazz. chim. ital.*, **41**, II, 603 (1911).

[24] (a) German Patent 175,070, *Friedländer*, **8**, 140 (1908); (b) German Patent 178,940, *Friedländer*, **8**, 756 (1908).

water by salting out with potassium chloride and washing as before. As thus purified it formed pale yellow lustrous crystalline flakes which decomposed near 240° without previous melting; yield, 5.1 g., or 60%.

In its analysis the potassium was determined by an adaptation of the process of Pregl,[25] and the sulfur by the Carius method.

*Anal.* Calcd. for $C_{13}H_9O_6S_2K$: C, 42.83; H, 2.49; K, 10.73; S, 17.51. Found: C, 43.21; H, 2.40; K, 10.49; S, 17.53.

This salt was insoluble or difficultly soluble in most of the commoner neutral organic solvents, but could be crystallized from a large volume of alcohol. Its solubility in cold water was low, but rose rapidly with rise in temperature. Concentrated sulfuric acid turned the crystals red and then slowly dissolved them to an orange solution. The salt appeared to be stable in 2 *N* sulfuric acid. In 0.5 *N* caustic alkali it dissolved to an orange solution.

This thiosulfate was treated with an equal weight of 2-amino-5-dimethylaniline thiosulfuric acid in a 20% sodium carbonate solution and oxidized by the air, following the process of the patent and the method used by Heller, Quast and Blanc[26] for the synthesis of Brilliant Alizarine Blue. These latter authors found that the thiosulfuric acid of hydroquinone gave more than one product when carried through this condensation, and our experience with the thiosulfuric acid described above was similar, the product consisting chiefly of deep reddish violet crystals mixed with a bluish black amorphous solid. The reddish violet crystals dissolved in glacial acetic acid, acetone or nitrobenzene to a bluish solution, and in benzene to a reddish violet one. The fact that a violet dye, presumably a thiazine, was formed in this condensation argues in favor of the assumption that in the original benzoylhydroquinone thiosulfuric acid the benzoyl was not adjacent to the thiosulfuric group.

**Hydroquinone dibenzoate,** $C_6H_4(OCOC_6H_5)_2$, was prepared from hydroquinone and benzoyl chloride, as described by Doebner and Wolff,[6] who gave the melting point as 199°. Our product crystallized from toluene in large flat needles, which were washed with hot alcohol and dried, and then melted at 204° (corr.); yield, 90%.

**Dibenzoylhydroquinone** $(C_6H_5CO)_2C_6H_2(OH)_2$.—Doebner and Wolff[6] reported the synthesis of this compound from hydroquinone dibenzoate and two moles of benzoyl chloride in the presence of small amounts of anhydrous aluminum chloride, at 190–200°, followed by hydrolysis of the product. All attempts to repeat this work, following carefully the rather vague and sketchy outline of the process as given by these investigators, resulted in excessive charring and a yield of pure product amounting to about 2%.

Böeseken[27] has reported that benzoyl chloride was decomposed by anhydrous aluminum chloride above 170° but, on studying this matter further, it was learned that considerable decomposition occurred at temperatures as low as 160°. The cause of the extensive charring in this dibenzoylhydroquinone synthesis was probably due, at least in part, to this decomposition of the benzoyl chloride, yet when the reaction was conducted at 165–175°, or at 175–185°, the charring increased and only a trace of the diketo derivative was obtained, whereas if the temperature was maintained at 200–205° and the aluminum chloride was added in small portions and at sufficiently wide intervals of time as to insure a slow and steady evolution of hydrogen chloride, the yield of the compound sought was raised to 12–15% of that calculated.

In this way a solution of 50 g. of hydroquinone dibenzoate in 49 g. of benzoyl chloride, kept at 200–205°, was treated with about 10 g. of aluminum chloride, in 0.5-g.

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[25] Pregl, Ref. 20, p. 135.

[26] Heller, Quast and Blanc, *J. prakt. Chem.*, [2] **108**, 257 (1924).

[27] Böeseken, *Rec. trav. chim.*, **27**, 10 (1908).

portions, until at the end of forty-eight hours the reaction was complete. The black tarry product when cold was treated with 300 cc. of 15% alcoholic potassium hydroxide, the mixture boiled for two hours, the alcohol distilled off, the residue treated with water, filtered and the blood red filtrate saturated with carbon dioxide. The diketo compound precipitated mixed with brownish impurities (mainly aluminum compounds). It was collected, washed with water and with 1 *N* hydrochloric acid, dried (weight, 8 g.) and recrystallized from alcohol in the presence of norite until the melting point remained constant at 210.5–211.1° (corr.). It formed fine yellow needles; yield, 12–15%. Doebner[28] gave the melting point as 206°, when crystallized from alcohol, and 207° from toluene.

The substitution of anhydrous ferric chloride for part or all of the aluminum chloride in this synthesis, or the use of nitrobenzene as solvent, seemed to do more harm than good.

Following the experiments of Klinger and Standke[15] for the production of monobenzoylhydroquinone from benzoquinone, a small quantity of monobenzoyl-*p*-benzoquinone was dissolved in excess of benzaldehyde and the solution exposed to direct sunlight. After standing for many days the solution became quite dark, but no crystalline material separated, and the experiments were discontinued.

Although it seemed highly probable that in this dibenzoyl derivative the two benzoyl groups were in the para relation to each other, because of the strong ortho-orienting influence of the hydroxyl groups, some experiments were carried out in the hope of obtaining practical proof of the truth of this assumption.

Efforts to reduce the two benzoyl groups to hydrols by the use of sodium amalgam, in either alkaline, alcoholic or glacial acetic acid solution, failed to give the desired product, although Doebner[28] successfully reduced *p*-benzoylphenol to the benzohydrylphenol in this way.

Doebner also obtained *p*-hydroxybenzoic acid from *p*-benzoylphenol by fusion with caustic alkali, but dibenzoylhydroquinone was instantly decomposed by such treatment.

Attempts to obtain bromine derivatives likewise proved fruitless, irrespective of variations in solvent, temperature or other factors.

**Dibenzoylhydroquinone Dimethyl Ether,** $(C_6H_5CO)_2C_6H_2(OCH_3)_2$.—To a solution of 2 g. of dibenzoylhydroquinone in 40 cc. of 20% sodium hydroxide, 10 cc. of methyl sulfate was added slowly while the solution was stirred vigorously, and well cooled until the end of this addition, when it was permitted to rise to about 50°. The original blood red color of the solution changed to yellow and a pale yellowish precipitate separated. Excess of methyl sulfate was destroyed by addition of more alkali and heating at 100°. The precipitate was collected and crystallized from either alcohol or glacial acetic acid, when it appeared in colorless dendritic flakes, m. p. 124–124.5°; yield, nearly that calculated.

*Anal.* Calcd. for $C_{22}H_{18}O_4$: C, 76.26; H, 5.24. Found: C, 75.61; H, 5.08.

It was insoluble in cold or in hot 10% sodium hydroxide. Heated for half an hour with two parts of constant-boiling hydriodic and one of glacial acetic acid, it was smoothly demethylated to the original dibenzoylhydroquinone.

An attempt to prepare this dimethyl ether by further benzoylation of the monobenzoyl dimethyl ether resulted in the elimination of the methyl from the methoxyl in Position 2, as already noted, and no dibenzoyl derivative was obtained.

**Dibenzoyl-*p*-benzoquinone,** $(C_6H_5CO)_2C_6H_2O_2$.—A solution of 4 g. of dibenzoylhydroquinone in 75 cc. of warm glacial acetic acid was oxidized by a mixture of 10 g. of sodium dichromate, 10 cc. of concentrated sulfuric acid and 250 cc. of water, in

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[28] Doebner, *Ann.*, **210**, 246 (1881).

essentially the same way as already described for the oxidation of the monobenzoylhydroquinone. The crude product was crystallized from a large volume of ligroin (b. p. 100–108°) and was thus obtained in orange needles, m. p. 164–164.5° (corr.); yield, 2.3 g., or 60%. This crystallization encountered the same obstacles that were noted for the monobenzoyl derivative and hence had to be carried out with similar precautions.

*Anal.* Calcd. for $C_{20}H_{12}O_4$: C, 75.93; H, 3.83. Found: C, 75.80; H, 3.94.

It was more or less soluble in most of the common neutral organic solvents and was moderately soluble in hot water with formation of a reddish orange solution. Toward caustic alkali it was much more stable than the monobenzoyl quinone. It was easily oxidized by cold alkaline permanganate and more slowly by chromic acid mixture. In both cases the product was benzoic acid. By sulfurous acid it was readily reduced to the original hydroquinone. With hydroxylamine its behavior was much the same as that of the monobenzoyl quinone, indicating that it too probably functioned as an oxidizing agent.

**Monoanilino-dibenzoylhydroquinone,** $(C_6H_5CO)_2(C_6H_5NH)C_6H(OH)_2$.—When a solution of 0.45 g. of dibenzoyl quinone in warm glacial acetic acid was treated with 0.4 g. of aniline in the same solvent, fine glistening scales soon separated from the dark solution and this separation was complete after thirty minutes' standing. The greenish yellow crystals were removed, washed with glacial acetic acid, then with alcohol, dried and recrystallized from alcohol, when they appeared as fine lustrous yellow plates, which became orange at about 225°, decomposed slightly at about 228°, and melted at 234.9–236.8° (corr.); yield, 0.3 g., or 52%.

*Anal.* Calcd. for $C_{26}H_{19}O_4N$: C, 76.25; H, 4.68. Found: C, 76.33; H, 4.66.

The compound dissolved slowly in cold dilute caustic alkali, but quickly in the hot to a deep orange solution which changed to yellow as it cooled.

Although we varied the conditions under which the quinone and aniline were brought together, we failed to isolate any product corresponding to that obtained from the Pechmann Dye and aniline and which Kozniewski and Marchlewski[4] believed to be a dibenzoylquinone dianilide, $(C_6H_5CO)_2C_6H_2(=NC_6H_5)_2$.

**Dibenzoylhydroxyhydroquinone triacetate,** $(C_6H_5CO)_2C_6H(OCOCH_3)_3$, was prepared from the dibenzoyl quinone (1 g.), acetic anhydride (3 g.) and a few drops of concentrated sulfuric acid, as described for the monobenzoyl compound. After standing for a few minutes at 40–50°, the orange color of the solution faded to pale yellow. It was poured upon cracked ice and left long enough to hydrolyze the excess of acetic anhydride without decomposing the readily hydrolyzable triacetate. The pale yellow oily product finally congealed to a nearly colorless solid, which was removed, washed with water, then with 50% alcohol, dried and crystallized from alcohol. It formed colorless glistening flakes, m. p. 120–120.5° (corr.); yield, 0 9 g., or 62%.

*Anal.* Calcd. for $C_{26}H_{20}O_8$: C, 67.79; H, 4.38. Found: C, 67.85; H, 4.44.

The product was insoluble in cold dilute caustic alkali, but dissolved in it when hot, with simultaneous hydrolysis and formation of an orange solution.

**Dibenzoylhydroxyhydroquinone,** $(C_6H_5CO)_2C_6H(OH)_3$.—A solution of 0.5 g. of the above triacetate in 5 cc. of alcohol containing 0.5 cc. of concentrated hydrochloric acid was heated for an hour at 100° and the resultant deep yellow solution diluted with an equal volume of water. As the solution cooled fine needles of the hydroxyhydroquinone separated in nearly theoretical yield. Recrystallized from 50–60% alcohol, rosets of yellow needles were obtained, m. p. 196.9–197.5°; yield, 0.3 g., or 83%.

*Anal.* Calcd. for $C_{20}H_{14}O_5$: C, 71.83; H, 4.22. Found: C, 71.47; H, 4.21.

This trihydric phenol dissolved in dilute caustic alkali to an orange solution, which was quite stable toward air oxidation, for after standing for several minutes in the air acidification precipitated the unaltered original phenol.

### Comparative Oxidation and Reduction Reactions of the Benzoylhydroquinones and Benzoylquinones

**Acid Oxidation of the Benzoylhydroquinones.**—Oxidation of the two hydroquinones with the same dilute chromic acid mixture, under identical conditions, showed that the dibenzoyl derivative was much more difficult to oxidize and considerable of the original hydroquinone was recovered unchanged.

**Alkaline Oxidation of the Benzoylhydroquinones.**—When dilute blood red alkaline solutions of equimolar concentrations of the two hydroquinones were exposed to the air for a short time and then acidified with dilute mineral acid, the original yellow hydroquinones were precipitated unaltered. On longer exposure of these solutions, however, that containing the monobenzoyl derivative turned dark brown before the color of the other underwent any change at all, and acidification of the two solutions precipitated only the dibenzoyl derivative unaltered. When these same original alkaline solutions were protected from the air, both were quite stable for the periods of time used in the experiments just mentioned.

Similar results were noted when hydrogen peroxide was used, in place of air, as the oxidizing agent. Dark brown solutions were obtained in both cases, but the original blood red color of the alkaline monobenzoyl solution changed much sooner than that of the dibenzoyl derivative. From both of these brown solutions, acidification precipitated a pale brown solid, from which benzoic acid was the only product isolated. The corresponding quinones may have been formed as intermediate products in this oxidation, but they were not detected and may have been changed as rapidly as formed to benzoic acid by the alkaline oxidizing medium.

**Reduction of Mono and Dibenzoylquinones.**—Equimolar concentrations of the two quinones in glacial acetic acid were treated with saturated sulfurous acid under identical conditions. Both quinones were thus reduced to their hydroquinones, but the reduction was more rapid and more nearly complete (for the same time interval) with the dibenzoyl than with the monobenzoyl derivative. This is in harmony with the oxidation experiments recorded above and indicates that the dibenzoylquinone has the greater affinity for hydrogen and hence probably the higher reduction potential.

**Tinctorial Properties of the Mono- and Dibenzoylquinones.**—Some unbleached wool was heated for thirty minutes at 100° in a 3% solution of monobenzoyl quinone in glacial acetic acid. The wool was dyed a dark reddish shade, while the dye bath retained its original yellowish orange color. Washed thoroughly with warm glacial acetic acid, then hot water and dried, the dyed wool appeared reddish-brown. This dyeing was quite fast to washing and to acid, but not to light, stoving, bleaching or alkali.

Similar experiments carried out with the dibenzoyl quinone gave similar results, except that the shade produced was more reddish and less intense and the dyeings rather less fast.

Because of the depth and richness of the color of the dianilino derivative of the monobenzoylquinone and its great stability toward acids, alkalies and other reagents, attempts were made to obtain fast dyeings by precipitating this compound within the fibers of the cloth. Unbleached wool was treated therefore with a 5% solution of the monobenzoyl quinone in glacial acetic acid and a solution of aniline in the same solvent was then added to this impregnated wool. The fabric was dyed a reddish shade, but much paler than the dye bath even after warming for an hour at 100°. In other experiments conditions were varied but the dyeings remained unsatisfactory in depth and quality.

## Summary

1. Benzoylated *p*-benzoquinones have been synthesized and studied, with results which support the constitutional formulas determined by Bogert and Ritter for the "Pechmann Dyes," rather than those proposed by Kozniewski and Marchlewski.

2. The acylated quinones represent a group hitherto unknown; their properties are therefore of interest.

3. Methods have been developed for the production of benzoylhydroquinones, which compounds are oxidized readily to the corresponding quinones.

4. The behavior of the benzoylquinones with aniline and with acetic anhydride has been studied and benzoyl hydroxyhydroquinones have been obtained.

5. Tests of the comparative stability of mono- and dibenzoyl quinones to oxidizing and reducing agents have been conducted, and some interesting problems concerning the structure of the benzoylhydroquinones are pointed out.

6. The synthesis and properties of other new compounds are described.

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