

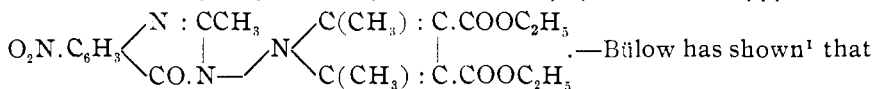
By fusing anthranilic nitrile with the nitroacetanthranil, and extracting the product with ether, heavy red needles were obtained, m. p.  $225^{\circ}$  (uncor.).

In a second experiment, the condensation was carried out in boiling nitrobenzene solution. The reddish crystals were treated with bone-black in benzene solution, and recrystallized from alcohol. Slender, glistening, yellowish needles, m. p.  $234^{\circ}$  (cor.); soluble in alcohol, benzene, ether, nitrobenzene or acetic anhydride.

Nitrogen found, 18.23 and 18.45. Calculated for  $C_{16}H_{10}O_3N_4$ : N, 18.30.

Long boiling with 95 per cent. alcohol changed this compound completely to the amide mentioned above, from which it could, as stated, be regenerated by dehydration with acetic anhydride. As anthranilic nitrile itself is rather resistant to hydrolysis, the ease with which this quinazolone nitrile changes to the amide is rather surprising.

*7-Nitro-2-methyl-4-quinazolonyl-3-(2,5-dimethyl-3,4-dicarbethoxy pyrrole)*,



hydrazines of the type  $RNHNH_2$  or  $R_2NNH_2$  condense with diacetosuccinic ester to derivatives of pyrrole.

Three grams of the 3-aminoquinazolone and four of ethyl diacetosuccinate were dissolved in 40 cc. of glacial acetic acid, the solution boiled for three hours, and then concentrated. A small amount of precipitate separated on cooling. This was removed, and alcohol added to the mother liquor. A white precipitate resulted, which was purified by repeated crystallization from alcohol, until it appeared in colorless, shining, minute scales, of a constant m. p. of  $171^{\circ}$  (cor.).

Found: C, 56.45; H, 4.8; N, 12.86. Calculated for  $C_{21}H_{22}O_7N_4$ : C, 57.0; H, 4.97; N, 12.67.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,  
NEW YORK, February 25, 1908.

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

## ON THE ACTION OF $\alpha$ -BENZOYLPHENYLHYDRAZINE ON THE HALOGEN DERIVATIVES OF QUINONES,

BY WILLIAM MCPHERSON AND WILBUR L. DUBOIS.

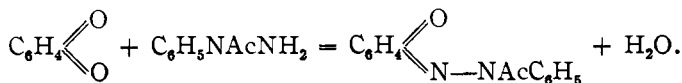
Received March 26, 1908.

The action of phenylhydrazine on quinones was first investigated by Zincke.<sup>2</sup> He showed that phenylhydrazine, as well as its salts, acted

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

<sup>2</sup> *Ber.*, 16, 1563.

energetically on the quinones of the benzene series with evolution of gas, but did not isolate the compounds formed. More recently it was shown by one of us, working under the guidance of Dr. J. U. Nef, that if the  $\alpha$ -hydrogen in phenylhydrazine is displaced by an acyl group the resulting compounds condense smoothly with benzo- and naphthoquinones in a perfectly normal manner, forming hydrazones.<sup>1</sup> Thus, with benzoquinone, the action is expressed by the following equation:



The action of naphthylhydrazine on both benzo- and naphthoquinones has also been studied by McPherson and Gore,<sup>2</sup> and the results of these investigations have had an important bearing in determining the constitution of the hydroxyazo compounds.

Zincke also studied the action of phenylhydrazine on the halogen derivatives of the benzoquinones<sup>3</sup> and found that decomposition occurred, accompanied by evolution of nitrogen. An investigation was begun in this laboratory to determine the action of acylated phenylhydrazines on the halogen derivatives of the quinones, and a preliminary paper was published.<sup>4</sup> Unfortunately the notes on all the work done were destroyed by the burning of the laboratory, and it has been possible only recently to resume again the investigation. Since a number of other investigators are working in this field, the following report is published with the hope that I may be allowed to reserve this phase of the subject for investigation. The action of the  $\alpha$ -acylated phenylhydrazines on the more recently discovered orthobenzoquinone, as well as its halogen derivatives, is also being studied with the hope that some light may be thrown on the constitution of the hydroxyazo compounds.

It has been found that the  $\alpha$ -acylated phenylhydrazines act on the halogen derivatives of the benzoquinones in three different ways, as follows:

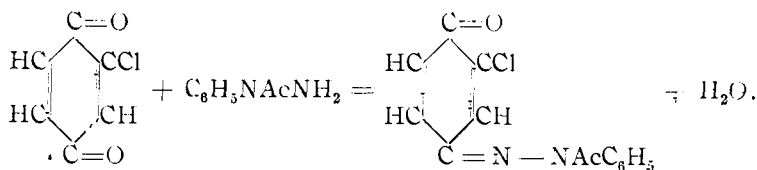
1. A regular condensation may take place with the formation of hydrazones. One would naturally expect this reaction with the monohalogenated quinones, since it is with these derivatives that hydroxylamine most readily condenses to form oximes. So far as the experiments have been carried out, it is only with these derivatives that hydrazones are formed. With monochlorbenzoquinone the reaction is expressed as follows:

<sup>1</sup> *Ber.*, 28, 2414; *Am. Chem. J.*, 22, 364.

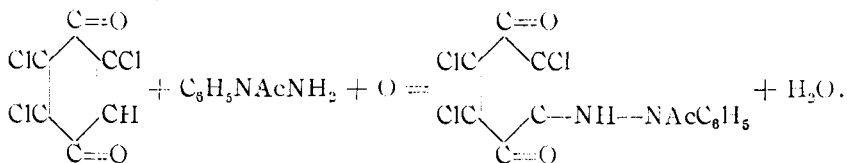
<sup>2</sup> *Am. Chem. J.*, 25, 485.

<sup>3</sup> *Ber.*, 16, 1563.

<sup>4</sup> THIS JOURNAL, 22, 141.

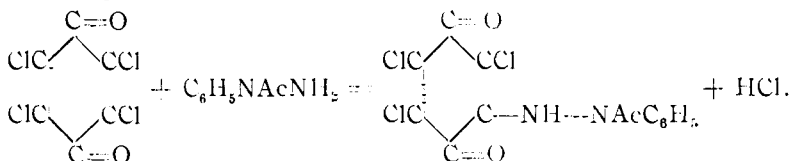


2. One of the hydrogen atoms in the  $\text{NH}_2$  group of the hydrazine, together with one of the atoms of the quinone hydrogen, may be removed by the oxidizing action of a second molecule of the quinone. Thus with trichlorquinone the action is as follows:



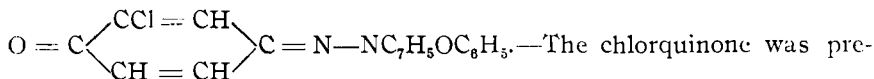
This reaction is in accord with the fact that hydroxylamine, which readily forms oximes with the monohalogenated quinones, does not do so with the trihalogen derivatives.

3. One of the hydrogen atoms in the  $\text{NH}_2$  group of the hydrazine may combine with a chlorine atom of the quinone, splitting off hydrochloric acid. Thus, with tetrachlorquinone, the reaction is expressed by the following equation:



### Experimental Part.

*Action of  $\alpha$ -Benzoylphenylhydrazine on Monochlorbenzoquinone. Monochlorquinonebenzoylphenylhydrazone,*



The chlorquinone was prepared from chlorhydroquinone by Clark's method.<sup>1</sup> Twenty-five grams of the chlorhydroquinone gave 20 grams of the chlorquinone when treated with the reagents in the following proportion: Chlorhydroquinone 25 g., manganese dioxide 36 g., water 125 cc., sulphuric acid 25 cc.

Five and four-tenths grams of the chlorquinone and 10 grams of  $\alpha$ -benzoylphenylhydrazine sulphate were dissolved by heating in separate portions of a mixture of 200 cc. of alcohol and 50 cc. of water. The solutions were cooled to room temperature and then mixed and heated slowly on a water-bath to from 50° to 60°, the mixture being stirred occasion-

<sup>1</sup> *Am. Chem. J.*, **14**, 555.

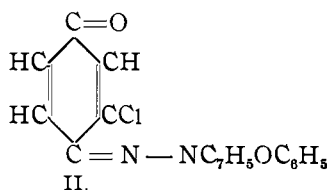
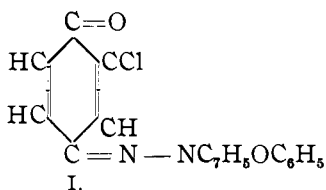
ally. As the temperature rose a yellow solid separated in the form of short, lath-shaped crystals. The mixture was set aside until it had acquired the room temperature and the solid was filtered off. A yield of 6 grams was obtained. The product was nearly pure, and after two crystallizations from benzene-ligroin melted sharply at  $172.5^\circ$  and gave the following results on analysis:

Calculated for  $C_{19}H_{13}N_2O_2Cl$ : C, 67.72; H, 3.89; N, 8.34; Cl, 10.53.  
 Found: C, 67.70; H, 4.15; N, 8.28; Cl, 10.02.

Monochlorquinonebenzoylphenylhydrazone is a yellow, crystalline compound very difficultly soluble in alcohol and ether. It readily dissolves in chloroform and benzene. From benzene it separates in rhomboids with faces almost equal in length, while from chloroform it separates in rhomboids having one axis greatly elongated. It is almost insoluble in ligroin and can best be purified by adding ligroin to a concentrated benzene solution. Phenylhydrazine acts upon it with evolution of nitrogen, although the action is not so energetic as with the corresponding non-halogenated benzoquinonehydrazone.

*Action of Saponifying Agents on Monochlorquinonebenzoylphenylhydrazone.*—The hydrazone was saponified by adding sulphuric acid and stirring until complete solution took place. The solution was then added slowly to water (not the reverse) when a yellow compound was formed, which collected on stirring. This was filtered, dried and purified by dissolving in ligroin. It separated from the ligroin in yellow, lath-shaped crystals, melting at  $86^\circ$ . The compound was soluble in sodium hydroxide and corresponded in properties to an hydroxyazo compound.

*Constitution of Monochlorbenzoquinonephenylhydrazone.*—In accordance with the method of preparation, the hydrazone must have one of the following formulas, depending upon whether the hydrazine condenses with the oxygen atom in the ortho or in the meta position to the chlorine.



It has been shown that when the corresponding non-halogenated compounds are saponified, hydroxyazo compounds are formed, the hydrogen which replaces the benzoyl group probably migrating from the nitrogen to the oxygen.

Now if formula I is correct, then on saponification one would expect to obtain benzeneazoorthochlorphenol, while if formula II is correct, then the corresponding benzeneazometachlorphenol would be formed. One

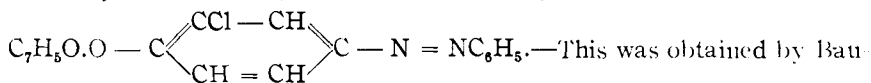
would naturally expect formula I to be the correct one, since it has been shown that hydroxylamine condenses by preference with the oxygen atom in the meta rather than in the ortho position to the chlorine. Accordingly, benzeneazoothochlorphenol was prepared. The following method gave a good yield and a fairly pure product:

Three grams of orthochlorphenol were dissolved in a solution of 7 grams of sodium hydroxide in 100 cc. of water, and the resulting solution diluted to 1000 cc. To the cold solution was added a solution of benzene diazonium chloride made by diazotizing 3.36 grams of aniline dissolved in 15 grams of concentrated hydrochloric acid and 30 cc. of water with 2.61 grams of sodium nitrite dissolved in 20 cc. of water. The resulting solution remained clear. On neutralizing with dilute hydrochloric acid, the hydroxyazo compound separated. It was purified by repeated crystallizations from ligroin, from which it separated in from brown to yellow lath-shaped crystals.

Calculated for  $C_{12}H_9N_2OCl$ : C, 61.47; H, 3.90; N, 12.07.  
Found: C, 61.20; H, 4.19; N, 12.27.

The benzeneazoothochlorphenol so prepared is identical with the product obtained by the saponification of chlorbenzoquinonebenzoylphenylhydrazone. Each of the compounds, as well as a mixture of the two, melt at  $86^\circ$ . Each, when benzoylated by the Baumann reaction, give identical benzoyl derivatives, melting at  $109^\circ$ . Hence, formula I, given above for the hydrazone, must be the correct one.

*Benzoyl Derivative of Benzeneazoothochlorphenol.*



mann's reaction. After adding the benzoyl chloride, the mixture was thoroughly shaken and allowed to stand until the oily precipitate solidified. The product was easily purified by crystallization from alcohol.

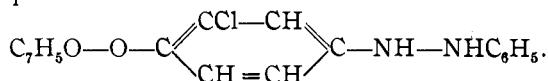
Calculated for  $C_{19}H_{13}N_2O_2Cl$ : C, 67.72; H, 3.89; N, 8.34.  
Found: C, 67.34; H, 3.99; N, 8.62.

Benzoylbenzeneazoothochlorphenol is a reddish yellow compound melting at  $109^\circ$ . It is very soluble in hot alcohol and the solution, on cooling, becomes almost solid with a mass of curved, hair-like crystals. It is very soluble in benzene and moderately so in ether, separating from the former in clusters of feather-like crystals and from the latter in clusters of needles. It is *not identical* but *isomeric* with chlorbenzoquinonebenzoylphenylhydrazone. The hydroxyazo compound contains the benzoyl group joined to oxygen, while in the hydrazone the benzoyl group is joined to nitrogen.

*Action of Reducing Agents on the Two Isomeric Benzoyl Derivatives.*

The hydroxyazo compound was dissolved in acetic acid, the solution cooled

and zinc dust added; the solution at once became clear. The zinc dust was removed by filtration. On adding water to the filtrate a white precipitate was obtained, which, after purification from benzene-ligroin, melted at from 157–158°. This was dissolved in alcohol and a few drops of a solution of ferric chloride added. On standing, the original hydroxyazo compound was regenerated and separated from the alcohol in the characteristic curved, hair-like crystals. No analysis was made of the white compound obtained by the reduction, since its reactions show it to be the dihydro derivative of the original hydroxyazo compound of the following composition:



The isomeric hydrazone, when reduced in a similar way, gave an almost black solution from which, on the addition of water, a black solid separated. While this probably contained benzanilide, it was found impossible to get it sufficiently pure to determine its identity beyond any doubt.

*Conversion of Monochlorquinonebenzoylphenylhydrazone into Benzoyloxiazochlorphenol.*—Willstätter and Veraguth recently have described<sup>1</sup> a most interesting and important rearrangement of the acyl derivatives of quinonephenylhydrazones into the corresponding oxyazo compounds. By means of this reaction the chlorquinonebenzoylhydrazone described above is readily converted into the isomeric hydroxyazochlorphenol. The hydrazone was dissolved in absolute ether and heated for several hours with a small amount of anhydrous powdered potassium hydroxide, as described by Willstätter and Veraguth. The hydrazone was converted almost quantitatively into the isomeric oxyazochlorphenol, the benzoyl group migrating from the nitrogen to the oxygen.

*The Action of  $\alpha$ -Benzoylphenylhydrazone Sulphate on Monochlorquinone in a Solution of Glacial Acetic Acid. Benzeneazoorthochlorphenol Sulphate.*—Two grams of  $\alpha$ -benzoylphenylhydrazone sulphate and 5.5 grams of monochlorquinone were dissolved in separate portions of 40 cc. of glacial acetic acid. The solutions were cooled to room temperature, then mixed and slowly heated on the water-bath with occasional stirring. At about 60° a mass of dark red, silky needles separated. The mixture was set aside until cold and the crystals filtered off and dried. The resulting substance was insoluble in all the common organic solvents except hot glacial acetic acid and acetone, and only sparingly soluble in these. It was purified by washing repeatedly with hot benzene. The resulting compound melted with decomposition at 188°–190°. The properties of the compound were similar to the hydrochlorides of the hy-

<sup>1</sup> *Ber.*, 40, 1432.

droxyazo compounds described by Hewitt and Pope.<sup>1</sup> This led to the belief that it might be the sulphate of benzeneazochlorphenol. Water was poured over it, the mixture heated slightly and filtered. The resulting compound was found to be benzeneazoorthochlorphenol. The sulphuric acid in the water was determined.

Calculated for  $C_{12}H_9N_2ClO \cdot H_2SO_4$ :  $H_2SO_4$ , 30.09.  
 Found:  $H_2SO_4$ , 29.65.

The formation of this compound is undoubtedly due to the saponification of the hydrazone at first formed, the resulting oxyazo compound then combining with the sulphuric acid originally present in the hydrazine sulphate to form the corresponding sulphate. While the hydrochlorides of a number of the hydroxyazo compounds have been prepared, so far as I know, this is the first sulphate to be described. Other quinones gave similar results, so that this method of preparation would seem to be a general one for the preparation of the sulphates of the hydroxyazo compounds.

COLUMBUS, OHIO.

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**STUDIES IN NITRATION. II.<sup>2</sup>—MELTING POINT CURVES OF BINARY MIXTURES OF ORTHO- META- AND PARANITRANILINES: A NEW METHOD FOR DETERMINING THE COMPOSITION OF SUCH MIXTURES.**

BY J. BISHOP TINGLE AND H. F. ROELKER.

Received March 5, 1908.

During the last academic year the senior author, in conjunction with Dr. F. C. Blanck, carried out a somewhat extensive investigation of the nitration of *N*-substituted aniline derivatives. In the course of this work, the results of which have been awaiting publication, in the *American Chemical Journal* since the middle of August, 1907, the need was frequently felt for a simple, expeditious method for the determination of the composition of mixtures of the isomeric nitranilines. Moreover, for our purpose, it was necessary that the method should be applicable to relatively small quantities of material. The only processes of which we have been able to find descriptions in the literature consist of recrystallizations, accompanied, in some cases, by conversion of one or more of the nitranilines into some simple derivative. Apart from the question of their accuracy, such methods did not appeal to us because they certainly involve a considerable amount of labor, and probably demand for their successful operation a relatively large quantity of material.

Besides their differences in solubility, the nitranilines vary somewhat in color, in their strength as bases, and, quite widely, in their melting-

<sup>1</sup> *Ber.*, **30**, 1624.

<sup>2</sup> Bishop Tingle and Blanck, *Am. Chem. J.*, **36**, 605 (1906).