acid, $C_8H_{14}(OH)CO_2H$, must be a stereoisomer of hydroxylauronic acid. In order to obtain further light on this question isocampholactone has been subjected to oxidation. Three grams of the lactone were heated for 72 hours with nitric acid (sp. gr. 1.27) in a 50 cc. flask sealed to an upright condenser. The heating was continued till the oily layer of lactone disappeared, a little concentrated acid being added from time to time. The study of the products of the oxidation is still quite incomplete. The products thus far obtained are a lactone, $C_8H_{12}O_4$, an acid melting at 228°, probably camphononic acid, and a compound, probably a lactone, which melts at 111°.

The *lactone*, $C_8H_{12}O_4$, is the chief product of the oxidation. It partly sublimes into the condenser during the oxidation and the remainder separates in crystalline form on cooling the solution. It is quite volatile and crystallizes from ligroin in needles. It is moderately soluble in ligroin, more easily soluble in ether and benzene. It melts at 122° and boils at 272°. A part of the analyses were not very satisfactory, possibly because of a partial hydrolysis of the lactone group.

Calculated for $C_8H_{12}O_4$:	C, 55.79;	H, 7.03.
Found:	C, 56.09, 56.38, 55.89, 54.85;	H, 7.19, 7.01, 7.25.
	54.81, 54.9, 54.9	7.12, 7.24, 7.12, 6.95.

The analyses were made with four different preparations.

Victor Meyer determinations gave a molecular weight of 164, 176.6, 180, 175, 166.2; average, 172; calculated, 172.1.

The molecular weight found by the lowering of the freezing point of glacial acetic acid was 175.3.

When the lactone is warmed with a solution of barium hydroxide or of sodium hydroxide it dissolves and somewhat more than one equivalent of the alkali is neutralized but the results were not concordant or satisfactory. As the presence of two lactone groups is impossible in a compound of this formula, it seems probable that the compound is decomposed by the alkali.

The formation of camphononic acid in the oxidation, if confirmed, will, of course, point to the formula given above for isocampholactone. We do not, however, feel justified in drawing any conclusions with regard to its structure from the work done thus far.

URBANA, ILL.

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

THE ACTION OF UNSYMMETRICAL BENZOYLPHENYLHYDRAZINE ON ORTHOBENZOQUINONE.

BY WILLIAM MCPHERSON AND H. J. LUCAS.

Received January 4, 1908.

The action of the unsymmetrical acyl phenylhydrazines on parabenzoquinone has been shown[1] to be as follows:

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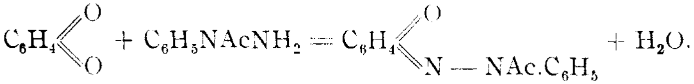
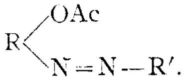
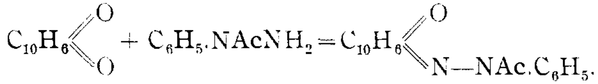
[1] *Ber.*, 28, 2414. *Am. Chem. J.*, 22, 364. THIS JOURNAL, 22, 141; 30, 816.



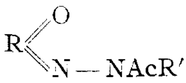
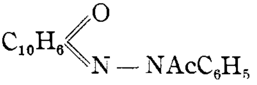
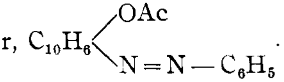
$$C_6H_4{<}\genfrac{}{}{0pt}{}{O}{O} + C_6H_5NAcNH_2 = C_6H_4{<}\genfrac{}{}{0pt}{}{O}{N - NAc.C_6H_5} + H_2O.$$

This reaction has been an important factor in the determination of the constitution of the parahydroxyazo compounds. Inasmuch as the hydrazones obtained by this reaction are not identical but isomeric with the corresponding acyl derivatives of the parahydroxyazo compounds, the proof is conclusive that in the latter compounds, the acyl group is joined to oxygen, and thus they have the general formula  $R{<}\genfrac{}{}{0pt}{}{OAc}{N = N - R'}$.

At the time the above work was carried out, the simplest orthoquinone, *viz.*, orthobenzoquinone had not been isolated. With β-naphthoquinone, the unsymmetrical acyl phenylhydrazines were found to condense and the reaction was represented by the following equation:



$$C_{10}H_6{<}\genfrac{}{}{0pt}{}{O}{O} + C_6H_5.NAcNH_2 = C_{10}H_6{<}\genfrac{}{}{0pt}{}{O}{N - NAc.C_6H_5}.$$

Inasmuch as the compounds so obtained are not isomeric but identical with the corresponding acyl orthohydroxyazo compounds, the latter were assigned the general formula  $R{<}\genfrac{}{}{0pt}{}{O}{N - NAcR'}$. The reaction was regarded as proof of the hydrazone character of these acyl orthohydroxyazo compounds. More recently, however, considerable doubt has been thrown upon the conclusions reached. Willstätter and Veraguth[1] have shown that the compounds obtained by the action of the unsymmetrical acyl phenylhydrazines on paraquinones, in which the acyl group is joined to nitrogen, easily undergo a rearrangement into the isomeric compounds in which the acyl group is joined to oxygen. The investigations of Goldschmidt and Löw Beer,[2] Auwers[3] and Auwers and Eckhardt[4] make it highly probable that in the reaction between β-naphthoquinone and the unsymmetrical acyl phenylhydrazines, the compound at first formed, *viz.*,  $C_{10}H_6{<}\genfrac{}{}{0pt}{}{O}{N - NAcC_6H_5}$, spontaneously rearranges as fast as formed into the isomer,  $C_{10}H_6{<}\genfrac{}{}{0pt}{}{OAc}{N = N - C_6H_5}$. If this be true, it is evident that the acyl derivatives of the orthohydroxyazo compounds, like the para derivatives are true hydroxyazo compounds and not hydrazones.

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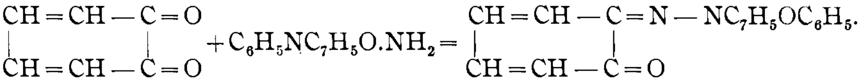
[1] *Ber.*, **40**, 1432.

[2] *Ibid.*, **38**, 1098.

[3] *Ibid.*, **40**, 2154.

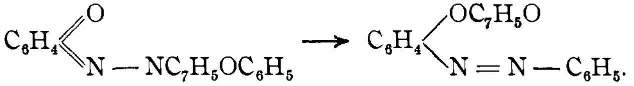
[4] *Ann.*, **359**, 336.

Recently the simplest of the orthoquinones, *viz.*, orthobenzoquinone has been isolated by Willstätter and Pfannenstiel,[1] and its properties studied. In order to obtain further evidence in regard to the constitution of the orthohydroxyazo compounds, we have studied the action of the unsymmetrical benzoylphenylhydrazine on orthobenzoquinone. This action may be expressed as follows:



$$\begin{array}{l} CH=CH-C=O \\ | \qquad\quad | \\ CH=CH-C=O \end{array} + C_6H_5NC_7H_5O.NH_2 = \begin{array}{l} CH=CH-C=N-NC_7H_5OC_6H_5. \\ | \qquad\quad | \\ CH=CH-C=O \end{array}$$

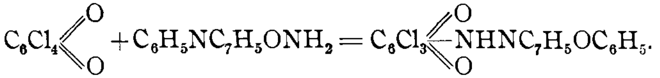
It is probable, however, that the hydrazone formed rearranges as fast as formed, as follows:



$$C_6H_4\begin{cases} O \\ N-NC_7H_5OC_6H_5 \end{cases} \longrightarrow C_6H_4\begin{cases} OC_7H_5O \\ N=N-C_6H_5. \end{cases}$$

The discussion of the constitution of the compound, however, is reserved until further work, now in progress, is completed. This compound, which we shall call benzoylorthohydroxyazobenzene, on saponification yields orthohydroxyazobenzene identical with the compound obtained by Bamberger.[2] When benzoylated, it yields a compound, *not isomeric but identical* with the original compound obtained by the action of unsymmetrical benzoylphenylhydrazine on orthobenzoquinone. The orthobenzoquinone is, therefore, completely analogous to β-naphthoquinone in its reaction with the unsymmetrical hydrazines.

With tetrachlororthobenzoquinone, the unsymmetrical benzoylphenylhydrazine reacts as follows:



$$C_6Cl_4\begin{cases} O \\ O \end{cases} + C_6H_5NC_7H_5ONH_2 = C_6Cl_3\begin{cases} O \\ NHNC_7H_5OC_6H_5. \\ O \end{cases}$$

A complete discussion of these reactions, however, is reserved for a further paper.

Experimental.

Action of Unsymmetrical Benzoylphenylhydrazine on Orthobenzoquinone.—The orthobenzoquinone was first prepared according to the method of Willstätter and Pfannenstiel. It was found, however, that the method described by Jackson and Koch[3] was not only much simpler but gave better results. The pyrocatechol was converted into the lead salt and thoroughly dried: 5 grams of this were treated with the theoretical amount of iodine dissolved in chloroform and stirred thoroughly. The resulting lead iodide was removed by filtration and the chloroform solution of orthobenzoquinone so obtained was treated with 4.5 grams of the unsymmetrical benzoylphenylhydrazine sulphate, previously ground

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[1] *Ber.*, 37, 4744.

[2] *Ibid.*, 33, 1939.

[3] *Am. Chem. J.*, 26, 10.

to a fine powder in chloroform. The mixture, on stirring, at once turned dark, but no evolution of gas could be detected. The chloroform was then removed by evaporation, and a tarry mass was left. This mass was extracted repeatedly with hot ligroin. The resulting ligroin solution, on standing, deposited nodules of microscopic orange-colored needles. The yield from 5 grams of the lead salt of pyrocatechol was about 0.7 gram. The compound was purified by repeated crystallization from ligroin. Analysis gave the following:

Calculated for $C_{19}H_{14}O_2N_2$: C, 75.44; H, 4.67; N, 9.29.
Found: C, 75.57; H, 5.00; N, 9.65.

Benzoylorthohydroxyazobenzene melts at 93°. It dissolves readily in benzene, separating in nodules. It is only slightly soluble in cold alcohol. From a hot alcoholic solution, it separates in thin plates. From an acetic acid solution, it separates in clusters of lath-shaped crystals. Its saponification is best effected by adding sodium hydroxide to a hot alcoholic solution. The resulting orthohydroxyazobenzene melts at 82–83°. While the yield is not large, the process is so easily carried out that it serves very well as a method for preparing orthohydroxyazobenzene.

The analogues of the above compounds have been prepared and their description together with a discussion of their constitution will be given in a later paper.

OHIO STATE UNIVERSITY, COLUMBUS, OHIO.

THE DETERMINATION OF TOTAL SULPHUR IN URINE.

BY OTTO FOLIN.

Received January 9, 1909.

In the January number of THIS JOURNAL F. W. Gill and H. S. Grindley published a paper under the above title, the essential conclusion of which is that the sodium peroxide method described by me in 1906[1] gives too low values for the total sulphur in urine and that the deficiency is due to loss of hydrogen sulphide. Gill and Grindley compare the results obtained according to my sodium peroxide method with results obtained by the nitric acid nitrate method published by Konshegg, and they assume that the higher values obtained by this later method come nearer being correct.

They further intimate that all sulphur determinations in proteins by means of alkaline fusion mixtures are probably too low because of losses of hydrogen sulphide.

A brief reply to the points raised by Gill and Grindley is, I think, called for.

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[1] *J. Biol. Chem.*, 1, 157 (1906).