into water-soluble products, and finally into glucose, but no evidence is at hand to show that the production of this sugar can be made quantitative.

The writer desires to reserve for a future paper the study of the reducing power, dyeing capacity, and hydrolysis of the celluloses precipitable from the reagents presented, in order to determin their relations to each other, to various other modified celluloses, and to the parent substance. A further study of the process of hydrolysis will be made to ascertain what substances are present in the final stage where glucose is produced. It is hoped that some of the reagents discussed may prove useful in separating and studying various modified celluloses.

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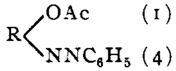
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE ACTION OF SUBSTITUTED HYDRAZINES ON β-ORTHOTOLUQUINONE.

BY WILLIAM MCPHERSON AND CECIL BOORD.

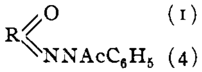
Received July 3. 1911.

Notwithstanding the many investigations carried on with a view of determining the constitution of the hydroxyazo compounds and their derivatives, the question still remains an open one, except in the case of the acyl derivatives of the members of the para series.[1] These derivatives are prepared by the action of the acyl chlorides or the corresponding anhydrides on the parent hydroxyazo compounds. The problem to be solved in connection with their constitution resolves itself simply into one of determining whether the acyl group is joined to oxygen or to nitrogen as indicated in the two following formulas:



$$R\Big\langle\begin{array}{ll}OAc & (1)\\ NNC_6H_5 & (4)\end{array}$$

Formula I.



$$R\Big\langle\begin{array}{ll}{=}O & (1)\\ NNAcC_6H_5 & (4)\end{array}$$

Formula II.

That formula I correctly represents the constitution of these derivatives was proved by the preparation of compounds having the constitution expressed in formula II. These compounds represented by formula II, in which the acyl group is joined to nitrogen, proved to be not identical but isomeric with the acyl derivatives of the corresponding parahydroxyazo compounds; hence in the latter compounds the acyl group must be joined to oxygen as shown in formula I above. The compounds of the type represented by formula II were prepared by the action of the unsymmetrical acylphenylhydrazines on the paraquinones as represented in the following equation:

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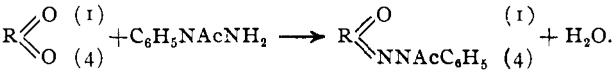
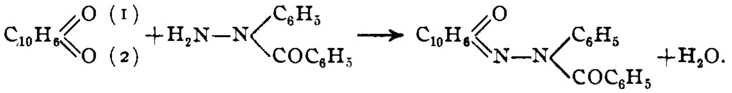
[1] McPherson, *Am. Chem. J.*, 22, 364; McPherson and Gore, *Ibid.*, 25, 485.



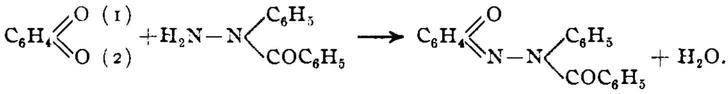
$$R\left\langle\begin{matrix}O & (1)\\ O & (4)\end{matrix}\right. + C_6H_5NAcNH_2 \longrightarrow R\left\langle\begin{matrix}O & (1)\\ NNAcC_6H_5 & (4)\end{matrix}\right. + H_2O.$$

This reaction has also been extended to the orthoquinones in the hope that the question of the constitution of the orthohydroxyazo compounds might be settled in a similar way. The action of the unsymmetrical benzoylphenylhydrazine on β-naphthoquinone[1] was first studied and the results were represented by the following equations:



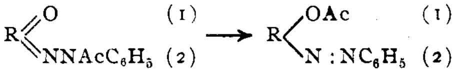
$$C_{10}H_6\left\langle\begin{matrix}O & (1)\\ O & (2)\end{matrix}\right. + H_2N-N\left\langle\begin{matrix}C_6H_5\\ COC_6H_5\end{matrix}\right. \longrightarrow C_{10}H_6\left\langle\begin{matrix}O\\ N-N\left\langle\begin{matrix}C_6H_5\\ COC_6H_5\end{matrix}\right.\end{matrix}\right. + H_2O.$$

Later the isolation of the simplest of the orthoquinones, *viz.* orthobenzoquinone,[2] made it possible to study the reaction between this compound and the unsymmetrical benzoylphenylhydrazine.[3] This reaction is expressed by the following equation:



$$C_6H_4\left\langle\begin{matrix}O & (1)\\ O & (2)\end{matrix}\right. + H_2N-N\left\langle\begin{matrix}C_6H_5\\ COC_6H_5\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}O\\ N-N\left\langle\begin{matrix}C_6H_5\\ COC_6H_5\end{matrix}\right.\end{matrix}\right. + H_2O.$$

These compounds prepared by the action of the unsymmetrical benzoylphenylhydrazine on orthoquinones can also be prepared by the action of benzoyl chloride on the corresponding orthohydroxyazo compounds. Thus the compound obtained by the action of the unsymmetrical benzoylphenylhydrazine on orthobenzoquinone is identical with that obtained by the action of benzoyl chloride on orthohydroxyazobenzene. The conclusion is, therefore, inevitable that either the acyl derivatives of the orthohydroxyazo compounds have the acyl group joined to nitrogen or that in the reaction between the unsymmetrical acylphenylhydrazines and the orthoquinones a migration of the acyl group takes place as represented by the following equation:



$$R\left\langle\begin{matrix}O & (1)\\ NNAcC_6H_5 & (2)\end{matrix}\right. \longrightarrow R\left\langle\begin{matrix}OAc & (1)\\ N:NC_6H_5 & (2)\end{matrix}\right.$$

That such a migration takes place is made probable from the observation of Willstätter and Veraguth[4] to the effect that the acyl derivatives of the parahydroxyazo compounds undergo a similar rearrangement when heated with a small amount of potassium hydroxide in ether solution. It would seem that if the para compounds undergo this rearrangement the ortho compounds would undergo a similar change with still greater ease. In fact it is entirely reasonable to suppose that in the case of the ortho compounds the rearrangement might take place spontaneously.

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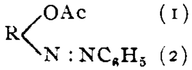
[1] McPherson, *Am. Chem. J.*, 22, 380.

[2] Jackson and Koch, *Am. Chem. J.*, 26, 10; Willstätter and Pfannesteil, *Ber.*, 1904, 4744.

[3] McPherson and Lucas, THIS JOURNAL, 31, 281.

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

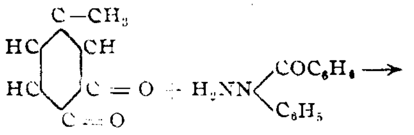
If it does not take place spontaneously, however, one would certainly expect it to take place under the same conditions which bring about the rearrangement of the para compounds. Yet these acyl derivatives of the ortho compounds undergo no change whatever under these conditions, even when heated for several hours. These facts lead to the conclusion that the acyl derivatives of the orthohydroxyazo compounds, like those of the para series, have the acyl group joined to oxygen and are therefore represented by the following formula:



$$R\begin{cases} OAc & (1) \\ N : NC_6H_5 & (2) \end{cases}$$

On the other hand when the benzoyl derivatives of orthohydroxyazobenzene are reduced a small percentage of benzanilide is formed as one of the reduction products. This would indicate that the benzoyl group is joined to nitrogen in the original compound; otherwise it is necessary to assume a migration of the benzoyl group from oxygen to nitrogen in the process of reduction. That such a migration is probable is shown by the investigations of Auwers and Eckardt.[1]

The difficulty attending the preparation of orthobenzoquinone in sufficient quantities to study its condensation products in detail led to an attempt to isolate other orthoquinones of the benzene series in the hope that some of these might be more readily prepared and more stable than the orthobenzoquinone itself. It was also hoped that some information might be obtained in regard to the probable migration of the acyl group in the acyl derivatives of the orthohydroxyazo compounds. It is entirely reasonable to suppose that the ease with which such a migration takes place would be influenced by the presence of other substituents in the benzene ring and it was hoped in this way to find some orthoquinone which would react with the unsymmetrical acylphenylhydrazines to form a compound sufficiently stable to admit of its isolation, in which compound the acyl group remained joined to nitrogen. The isolation of such a compound would definitly prove the constitution of the acyl derivatives of the orthohydroxyazo compounds. Our experiments have shown that β-orthotoluquinone ($CH_3 : O : O = 1 : 3 : 4$) is not only more readily prepared than the orthobenzoquinone itself but that it is much more stable. A specimen of it left under a glass dish in the laboratory for two months showed only a slight darkening in color at the end of that period. This quinone reacts with the unsymmetrical benzoylphenylhydrazine in accordance with the following equation:



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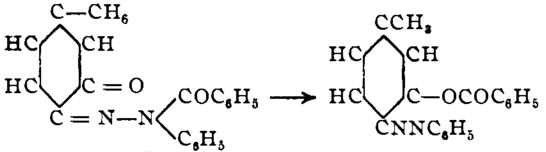
[1] *Ann.*, 359, 336.

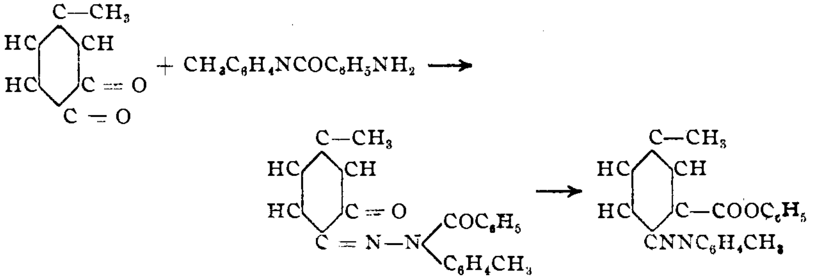


Formula I. Formula II.

That the resulting compound has the constitution expressed by formula II is shown by the following considerations. When saponified it yields benzeneazometacresol, $CH_3C_6H_3(OH)N_2C_6H_5(CH_3 : OH : N_2 = 1 : 3 : 4)$, which is isomeric with the corresponding para cresol described by Nölting and Kohn.[1] This proves that the hydrazine condenses with the oxygen which is in the para position to the methyl group in the quinone. That the acyl group is joined to oxygen rather than to nitrogen is made extremely probable from the fact that the compound undergoes no change whatever when dissolved in absolute ether to which a small amount of fused potassium hydroxide has been added and heated for several hours. Under these conditions the acyl group, if joined to nitrogen, should migrate to the oxygen atom as in the case of the corresponding para compounds. It is true on the other hand that when reduced with zinc dust and acetic acid, a very small percentage of benzanilide is formed; but the formation of this can be satisfactorily explained by the migration of the benzoyl group during reduction.[2] The particular interest in the reaction between the quinone and hydrazine was centered in the efforts to isolate the possible intermediate compound in which the benzoyl group is joined to nitrogen. All attempts to prove the formation of such a compound failed.

When benzeneazometacresol is benzoylated, there is formed benzeneazometacresol benzoate, identical in every respect with the product formed by the action of the unsymmetrical benzoylphenylhydrazine on the β-orthotoluquinone.

The action of the unsymmetrical benzoyltolylhydrazine on β-orthotoluquinone is similar to that of the corresponding phenylhydrazine and is represented by the following equation:



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[1] *Ber.*, **17**, 352.

[2] Auwers and Eckardt, *Ann.*, **359**, 336.

The resulting tolylazometacresol benzoate, when saponified, yields tolyl azometacresol of the following constitution: $C_6H_3(CH_3)(OH)(N_2C_6H_4CH_3)$(1 : 3 : 4).

Experimental Part.

Preparation of β-Orthotoluquinone.—The monomethyl ester of homocatechol (kreosol) was used as the starting material in the preparation of the quinone. This ester was saponified by the action of hydriodic acid at a high temperature as described by Cousins.[1] From 50 grams of the ester there were obtained 11 grams of pure homocatechol. From this the quinone was prepared in accordance with the general method used by Willstätter and Pfannenstiel[2] in the preparation of the orthobenzoquinone. Two and one-half grams of the homocatechol were dissolved in anhydrous ether and to the solution were added 10.5 grams of silver oxide and 8 grams of fused sodium sulfate. The mixture was shaken for one hour and then filtered. The garnet-red ethereal solution upon evaporation deposited reddish-brown crystals of β-orthotoluquinone. Before the ether had entirely evaporated the crystals were filtered off and washed with ligroin.

The quinone was also prepared by treating the lead salt of homocatechol with iodine according to the method used by Jackson.[3] Ten grams of the homocatechol were dissolved in two liters of water and heated almost to boiling. To this hot solution was added a solution of 30 grams of lead acetate. The lead salt separated out and was washed a number of times by decantation. 0.5 gram of the dried salt was suspended in 25 cc. of chloroform and to this was added a solution of 3.9 grams of iodine in 125 cc. of chloroform. The mixture was shaken for about 15 minutes and the lead iodide removed by filtration. The resulting filtrate deposited the quinone on evaporation but the product was not so pure as that prepared by the method of Willstätter and Pfannenstiel. A purer product was obtained by substituting absolute ether for chloroform in the above method.

Analysis: Calculated for $C_7H_6O_2$: C, 68.83; H, 4.95.
Found: C, 68.72: H, 5.31.

β-Orthotoluquinone is a reddish-brown solid, non-volatil and practically odorless. It is easily soluble in acetone, chloroform, methyl alcohol ether and benzene and is almost insoluble in ligroin. It melts at 70–75° with decomposition. From a benzene solution it separates in clusters of needles.

The Action of Unsymmetrical Benzoylphenylhydrazine on β-Orthotoluquinone: Benzeneazometacresol benzoate, $C_6H_3(CH_3)(OC_7H_5O)(N_2C_6H_5)$ *(1 : 3 : 4)*.—The following method gave the best results: Five grams

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[1] *Compt. rend.*, **115**, 234 and *Ann. chim. phys.*, **13**, 532.

[2] *Ber.*, **1904**, 4744.

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

of the lead salt of homocatechol were suspended in chloroform and iodine added as described above for the preparation of the quinone. The lead iodide was removed by filtration and the resulting filtrate added directly to a solution of 3.2 grams of unsymmetrical benzoylphenylhydrazine in chloroform. The resulting mixture at once turned dark and upon spontaneous evaporation deposited an oily tar. This tar was repeatedly extracted with petroleum ether and the combined extracts upon evaporation deposited tufts of yellow needles together with a reddish oil. The mass was stirred with cold methyl alcohol, which dissolved out the oil. The remaining crystals were further purified by crystallization from ligroin. In this way 2 grams of orange-yellow needles melting sharply at 98° were obtained.

Analysis: Calculated for $C_{20}H_{16}N_2O_2$: C, 75.91; H, 5.10.
Found: C, 75.69; H, 5.23.

Benzeneazometacresol benzoate is an orange-yellow solid, very slightly soluble in cold methyl and ethyl alcohol but readily so in hot ligroin and benzene.

The Reduction of Benzeneazometacresol Benzoate.—3.94 grams of the benzoate were dissolved in about 50 cc. of glacial acetic acid. Small portions of zinc dust were added from time to time and the mixture warmed. In a few minutes the solution became almost colorless. It was decanted from the zinc and poured into water (750 cc.). On stirring there soon separated a slightly pinkish solid. This was filtered off and treated with a very dilute solution of sodium hydroxide. There remained a residue of 0.15 gram which proved to be benzanilide. Upon acidifying the alkaline solution a white flocculent precipitate (1.11 grams) was formed, which when purified melted at 159–160°. The constitution of this compound is probably expressed by the following formula: $C_6H_3(CH_3)(OH)(NHC_7H_5O)(1 : 3 : 4)$.

Saponification of Benzeneazometacresol Benzoate:—Benzeneazometacresol, $C_6H_3(CH_3)(OH)(N_2C_6H_5)(1 : 3 : 4)$.—The benzoate was saponified by dissolving in cold concentrated sulfuric acid and pouring the resulting solution into water. Benzeneazometacresol separated out and was purified by crystallizing from hot ligroin.

Analysis: Calculated for $C_{13}H_{12}N_2O$: C, 73.58; H, 5.66.
Found: C, 72.97; H, 5.80.

Benzeneazometacresol ($CH_3 : N_2 = 1 : 4$) crystallizes from hot ligroin in thin red plates melting at 122°. It is readily soluble in alcohol, benzene, acetone and chloroform. Like the other known orthohydroxyazo compounds it is very slightly soluble in alkalies. It was benzoylated by dissolving in absolute alcohol containing the theoretical amounts of sodium ethylate necessary to form the sodium salt and then adding a slight excess of benzoyl chloride. The resulting benzoate was purified by crystallization, first from methyl alcohol and finally from ligroin. It proved to be identical with the original benzoate prepared by the action of the unsymmetrical benzoylphenylhydrazine on β-orthotoluquinone.

The Action of Unsymmetrical:—Benzoyltolylhydrazine on β-Orthotoluquinone:—Tolylazometacresol Benzoate, $C_6H_3(CH_3)(OC_7H_5O)(N_2C_6H_4CH_3)$ (*1 : 3 : 4*).—This reaction with the tolylhydrazine was carried out under the same condition as with the phenylhydrazine described above. There was thus obtained an orange colored solid melting at 93°.

Analysis:	Calculated for $C_{21}H_{18}N_2O_2$:	C, 76.36; H, 5.45.
	Found:	C, 75.71; H, 5.64.

Tolylazometacresol benzoate is slightly soluble in cold methyl and ethyl alcohol and readily so in hot benzene and ligroin. It is deposited from ligroin in the form of light orange colored needles. When dissolved in sulfuric acid and the resulting solution poured into water tolylazometacresol, $C_6H_3(CH_3)(OH)(N_2C_6H_4CH_3)$(1 : 3 : 4), was deposited as an orange-red solid which on crystallization from ligroin melted at 148°.

Analysis:	Calculated for $C_{14}H_{14}N_2O$:	C, 74.33; H, 6.19.
	Found:	C, 74.24; H, 6.13.

Tolylazometacresol readily dissolves in hot ligroin, crystallizing out in the form of thin lath-shaped crystals, orange-red in color. Like the other orthohydroxyazo compounds it is very slightly soluble in alkalies. It is isomeric with the paratolylazoparacresol, $C_6H_3(CH_3)(N_2C_6H_4CH_3)$ (OH)(1 : 3 : 4), described by Nölting and Kohn.[1] When benzoylated by dissolving in alcohol containing sodium ethylate and adding benzoyl chloride, tolylazometacresol benzoate is formed, identical with the compound formed by the action of the unsymmetrical benzoyltolylhydrazine on β-orthotoluquinone.

COLUMBUS, OHIO.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

HYDANTOINS: THE REDUCTION OF ALDEHYDE CONDENSATION-PRODUCTS OF 1-PHENYL-2-THIOHYDANTOIN.

[FOURTH PAPER.]

BY TREAT B. JOHNSON AND CHARLES A. BRAUTLECHT.

Received July 20, 1911.

In a previous paper from this laboratory, Wheeler and Hoffman[2] have described a new and practical method of synthesizing phenylalanine and tyrosine. They condense hydantoin with benzaldehyde and anisaldehyde, forming 4-benzal- and 4-anisalhydantoins respectively. When these unsaturated compounds are warmed with hydriodic acid they are reduced at the double bond and transformed quantitatively into the

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[1] *Ber.*, **17**, 354.

[2] *Am. Chem. J.*, **45**, 368.