

and their color seems to be dependent on the halogen content, the bromides being invariably red, and the chlorides yellow.

A solution of tellurium dioxide in halogen acids gives a precipitate with nearly all of the alkaloids, probably forming salts similar to those above described. The alkaloid derivatives are now being studied in this laboratory.

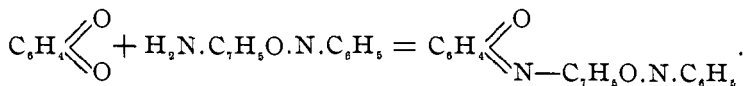
## THE ACTION OF $\alpha$ -ACYLATED PHENYLHYDRAZINES ON THE CHLORINE DERIVATIVES OF QUINONES.

(PRELIMINARY REPORT.)

BY WILLIAM MCPHERSON AND ROBERT FISCHER.

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THE investigations of Zincke<sup>1</sup> on the interaction of phenylhydrazine and the quinones led to the general result that  $\alpha$ -naphthoquinone,  $\beta$ -naphthoquinone, and phenanthraquinone condense in a normal manner with phenylhydrazine, but that under similar conditions, all of the quinones of the benzene series give hydroquinones, the reaction being attended with gas evolution. Many subsequent efforts have been made to effect a normal condensation between benzoquinone and phenylhydrazine, since this reaction would help to solve the problem of the constitution of the oxyazo-bodies. Although this has not as yet been accomplished, it has been shown by one of us<sup>2</sup> that the unsymmetrical acylated phenylhydrazines, *e. g.*,  $C_6H_5N.C_6H_5O.NH_2$ , condense with benzoquinone in a normal manner forming a hydrazone derivative in accordance with the following equation :

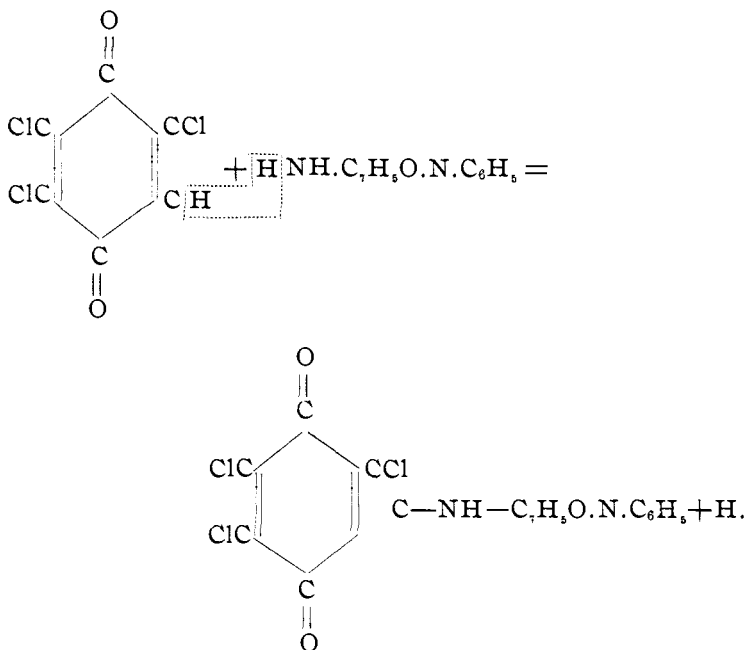


This reaction has recently been extended to the chlorine derivatives of quinone. It has been found, however, that while the  $\alpha$ -acylphenylhydrazines react with these readily, the compounds formed are not hydrazones but *hydrazino* derivatives, possessing a structure similar to the so-called anilidoquinones, formed by the interaction of quinones and aniline under certain conditions. With trichlorbenzoquinone the following reaction

<sup>1</sup> *Ber. d. chem. Ges.*, 16, 1563.

<sup>2</sup> *Ibid.*, 28, 2414; *Am. Chem. J.*, 22, 364.

takes place, the two hydrogen atoms being removed by the oxidizing action of a second molecule of the quinone.



This reaction is analogous to the interaction of trichloroquinone and aniline, investigated by Niemeyer,<sup>1</sup> the point of attack being the hydrogen of the quinone in preference to the chlorine.

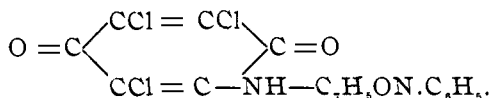
Tetrachloroquinone gives with  $\alpha$ -benzoyl phenylhydrazine the same product as trichloroquinone, hydrochloric acid being evolved.

It is quite probable that under different conditions, hydrazone derivatives of the chloroquinones may be obtained. This subject is now under investigation in this laboratory. The interaction of the quinones and the unsymmetrical naphthylhydrazine derivatives is also being studied with the hope of isolating both the true oxyazo-bodies and their isomeric quinonehydrazones and thus definitely deciding the constitution of the so-called free oxyazo-bodies.

<sup>1</sup> *Ann. Chem.* (Liebig), **228**, 322.

## EXPERIMENTAL PART.

*Action of  $\alpha$ -Benzoyl Phenylhydrazine on Trichlorbenzoquinone.*—  
 $\alpha$ -Benzoyl phenylhydrazino trichlorquinone,



The hydrazine was prepared according to Widman's excellent method,<sup>1</sup> for the preparation of unsymmetrical hydrazines. Some slight changes in the process were found advantageous. In the case of  $\alpha$ -benzoyl- $\beta$ -acetylphenylhydrazine the following method easily gives the pure solid product, in place of the difficultly solidifying oil which Widman first obtained. To 10 grams of pure  $\beta$ -acetylphenylhydrazine were added 70 grams of benzene and 9.4 grams of benzoyl chloride. The flask was connected with a return condenser and its contents heated to boiling. The hydrazine slowly dissolved with evolution of hydrochloric acid. After heating for a few minutes the  $\alpha$ -benzoyl- $\beta$ -acetylphenylhydrazine began to separate on the sides of the flask owing to the slight solubility of the body in benzene. After heating for one hour, the reaction was complete. On cooling, the product was removed by filtration, and was obtained pure (m. p.  $152^\circ$ – $153^\circ$ ) by a single crystallization from alcohol diluted with an equal volume of water. The yield is nearly quantitative. From this the difficultly soluble sulphate  $(\text{C}_6\text{H}_5\text{NC}_6\text{H}_5\text{O} \cdot \text{NH}_2)_2\text{H}_2\text{SO}_4$  was prepared by saponification as directed by Widman. In the first experiments the free base was obtained from this sulphate and then converted into the soluble hydrochloride. In the later experiments, however, it was found advantageous to use the original sulphate, dissolving it in water to which was added just enough alcohol to effect solution.

Four grams of trichlorquinone and 7 grams of  $\alpha$ -benzoylphenylhydrazine sulphate in a finely divided condition were placed in a flask and 300 cc. of water, 140 cc. of alcohol, and a few drops of sulphuric acid added. The flask was connected with a return condenser and the contents boiled for five minutes. The red powder which separated was then filtered from the hot liquid and dried on a clay plate (yield 5 to 6 grams). The body was

<sup>1</sup> Monograph "Ueber asymmetrische Secundäre Phenylhydrazine," published by the "Gesellschaft der Wissenschaften" at Upsala 1893; also *Ber. d. chem. Ges.*, 26, 945.

easily purified by crystallizing from benzene, or from benzene-ligroin. Melting-point  $158.5^{\circ}$ .

1. 0.1641 gram substance gave 0.1668 gram silver chloride.

2. 0.2115 gram substance gave 0.2127 gram silver chloride.

1. 0.2397 gram substance gave 0.4714 gram carbon dioxide and 0.0620 gram water.

2. 0.2484 gram substance gave 0.4891 gram carbon dioxide and 0.0619 gram water.

	Calculated for $C_{12}H_{11}N_2O_2Cl_3$ .	Found.	
		1.	2.
C .....	54.09	53.63	53.69
H .....	2.63	2.87	2.76
Cl .....	25.23	25.13	24.86

$\alpha$ -Benzoyl phenylhydrazino trichlorquinone is a bright red crystalline body, readily soluble in hot benzene and alcohol, from each of which it crystallizes in long rectangular prisms or in star-shaped groups of small prisms. It is sparingly soluble in ligroin, and practically insoluble in glacial acetic acid and dilute caustic soda solution. Its action with phenylhydrazine is similar to that of quinone, decomposition occurring with evolution of gas. By dissolving in concentrated sulphuric acid as well as by the action of alcoholic potash, the benzoyl group is split off, but some further reaction takes place forming a dark brown crystalline body. This is soluble in caustic soda and melts with decomposition at  $198^{\circ}$ . Its structure has not yet been determined.

OHIO STATE UNIVERSITY, JANUARY, 1900.

## NOTE ON A METHOD OF STANDARDIZING WEIGHTS.

BY THEODORE WILLIAM RICHARDS.

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ALTHOUGH nowadays it is possible to procure, for a comparatively small sum, sets of weights which are reasonably exact, it is recognized that for gravimetric work demanding any considerable degree of accuracy, corrections on account of occasional errors in the weights must be applied. It is obvious, moreover, that if the relative values of the weights in an inexpensive box are known, this set may serve a purpose which would otherwise demand a much more expensive one. For ten years every student in quantitative analysis at Harvard has been required to standardize his weights; and since the method