The ether extract was separated, evaporated, and the residue upon purification identified as triphenylcarbinol. The acid aqueous solution was placed in a separatory funnel, made alkaline, and shaken with ether. The aqueous extract was drawn off and soon smelled of methylhydroxylamine. The ether extract was shaken with a solution of one cc. of N/HCl in 5 cc. water, the acid extract was drawn off, and after having been made slightly alkaline, the addition of bleaching powder solution gave no test for methylaniline or aniline.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

OCTOIODOPARAQUINHYDRONE.[1]

BY C. LORING JACKSON AND E. K. BOLTON.

Received December 15, 1913.

The work described in this paper grew out of the suggestion of the late Professor H. A. Torrey that one of us (Bolton) should take up the study of iodoanil, begun by him and Dr. Hunter.[2] After the too early death of Professor Torrey the research was continued by us, and among other derivatives of iodoanil, the description of which will appear soon in another paper, we tried to make the corresponding octoiodoquinhydrone. For this purpose we exposed a benzene solution of iodoanil to the action of sulfurous acid at ordinary temperatures and, after four weeks, were rewarded by the appearance of glistening black crystals of considerable size. These differed in color from crystals of iodoanil (prepared from benzene for the sake of comparison), as the latter were brown, but both formed flattened prisms or long plates terminated by two planes at an obtuse angle, and, although slight differences appeared, they seemed to us more in habit than real crystalline form. It was therefore necessary to bring convincing proofs that these black crystals were not iodoanil but a new substance, and we think, these will be found in the following observations: Treatment of the black crystals with benzene and alcohol, toluene, or glacial acetic acid yielded in each case a yellow solution, from which, in addition to the brown crystals of iodoanil, a quantity of a white substance soluble in sodium hydroxide was obtained, which can hardly be anything but tetraiodohydroquinone. An aqueous solution of sodium hydroxide disintegrated the crystals, leaving a brown powder (iodoanil), and dissolving a white substance (tetraiodohydroquinone). Parallel experiments with iodoanil showed that the alkaline solution was without action under the same conditions, and that the organic solvents yielded only brown crystals with no white admixture whatever. The crystals

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton.

[2] THIS JOURNAL, 34, 702 (1912).

have therefore behaved like the quinhydrone which should be dissociated by solvents[1] or decomposed by sodium hydroxide into iodoanil and tetraiodohydroquinone.

A quantity of iodoanil was dissolved in benzene and submitted to the action of sulfurous acid at ordinary temperatures. The amount of solid in 50 cc. was determined at the beginning of the experiment, and again after the black crystals had been formed. The second determination yielded 0.1362 gram less solid than the first, showing that a substance less soluble than iodoanil had been formed and precipitated. The experiment was carried on in a tightly corked flask, the weight of which remained constant during the formation of the crystals. This seems to us an absolute proof that the black crystals are not iodoanil.

The behavior of the black crystals, when heated, also leads to the same conclusion, for they began to decompose at 190° with evolution of iodine, and did not melt even at much higher temperatures; whereas the iodoanil, from which the black crystals were obtained, began to soften at 260°, and melted at 265° with decomposition but no evolution of iodine.

The black crystals contained the amount of iodine required by the octoiodoquinhydrone, but the analysis has little significance, because iodoanil, or tetraiodohydroquinone, contains essentially the same percentage.

Although the quinhydrone could be prepared by the method described above and also by the action of iodoanil and tetraiodohydroquinone on each other in benzene solution, the yield was never large, and occasionally no reaction took place, so that it seems as if the two substances have but a slight tendency to combine to make the quinhydrone. But its formation, at all, is of interest, because it is the first paraquinhydrone containing 8 atoms of halogen which has been obtained. Staedeler,[2] it is true, thought that he made the octochloroquinhydrone by the action of ferric chloride, or nitric acid, on tetrachlorohydroquinone, but his product was yellow, and, therefore, could not have been the quinhydrone. The early date of this work (1849) accounts for his ignorance of the fact that a dark color is the essential character of these bodies. Our real knowledge of this subject is due to the thorough work of Ling and Baker,[3] who tried to prepare a quinhydrone from chloroanil under the most varied conditions, but without a sign of success, except when they boiled for 3 hours a xylene solution of chloroanil and tetrachlorohydroquinone and obtained dark violet prismatic needles; but in spite of the resemblance of these crystals to a quinhydrone, they proved that they were tetrachlorohydroquinone, colored by some impurity, since a quantitative oxidation gave re-

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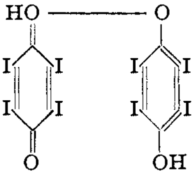
[1] Torrey and Hardenbergh, *Am. Chem. J.*, 33, 167 (1905).

[2] *Ann.*, 69, 329 (1849).

[3] *J. Chem. Soc.*, 63, 1323 (1893).

sults corresponding to this substance. They are of the opinion that the color is due to a trace of a quinhydrone, but one containing less than 8 atoms of chlorine, as this result was obtained with xylene purified only by distillation, which might contain some reducing impurity, while on repeating the experiment with xylene purified with sulfuric acid no dark color was observed. Ling and Baker's paper therefore establishes the fact that the octochloroquinhydrone is not formed under conditions which give quinhydrones easily with substances containing less halogen, so that, if it can exist at all, for which there is no evidence, it must be a very unstable compound. This conclusion is supported by an experiment of our own, in which chloroanil was exposed to the conditions, which had yielded the octoiodoquinhydrone, but there was no evidence whatever that any reaction had taken place; and a similar experiment with bromoanil gave the same result. So far as we have found, no other experiments have been tried with bromoanil, and, although this one indicates that like chloroanil it resists vigorously the formation of a quinhydrone, many more under varying conditions are needed before this property of bromoanil can be considered definitely established.

Richter[1] has proposed a theory for the constitution of the quinhydrones, according to which they are oxonium salts, so that our compound would have the formula



and he has pointed out that the difficulty in forming octohalogen quinhydrones was to be expected, since the negative radicals would reduce the basic character of the oxygen, on which the formation of the oxonium salt depends. Our discovery of an iodine compound, when those with chlorine and perhaps bromine could not be obtained, is certainly in harmony with this theory, as the less negative iodine would interfere with the formation of the oxonium salt less than either chlorine or bromine, but we cannot see that the other structural formulas proposed[2] for the quinhydrones would explain our observations.

The difficulty in forming octohalogenquinhydrones does not appear in the ortho series, as the tetrachloro-[3] or tetrabromoorthoquinone[4] forms

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[1] *Ber.*, 43, 3603 (1910).

[2] Jackson Oenslager, *Am. Chem. J.*, 18, 1 (1896); Valeur, *Ann. chim. phys.*, 21, 470 (1900); Posner, *Ann.*, 336, 85 (1904); Urban, *Monatsh.*, 28, 299 (1907); Willstätter, *Ber.*, 41, 1464 (1908).

[3] Jackson and P. W. Carleton, *Am. Chem. J.*, 39, 493 (1908).

[4] Jackson, Russe, *Ibid.*, 35, 174 (1906).

such a compound under varied conditions and with large yields. If the negative influence of the halogen is the only thing which stands in the way of the quinhydrone formation, this difference must be due to the differences in position of the halogen in the ortho and paraquinones. In trying to discover the effects of halogens in certain positions on basicity, we naturally turned to the halogen amino compounds, and were astonished at the meagerness of the material available. The two dibromoanilines, 1,2,6 and 1,2,4, were the only compounds known which seemed to us to furnish a serviceable analogy with the tetrahalogen para- and orthoquinones. The hydrochloride of the 2,6 compound[1] loses the acid easily by standing, in the air, and is decomposed by water. The 2,4 compound,[2] on the other hand, forms stable salts, which can be recrystallized. The inference from these observations is that the diorthohalogen (occurring in the paraquinone) has a greater influence on the basicity than the orthoparahalogen (as in the orthoquinone), and, while we find no entirely satisfactory confirmation of this view among the other known halogen amino compounds, there is certainly nothing opposed to it. In this single case, therefore, we have phenomena similar to those observed with para- and orthoquinones, if the quinhydrones are oxonium salts.

In the discussion given above it was assumed that the presence of halogens is the only condition which influences the formation of the quinhydrones, but it is probable that this is not the case. The mutual action of the two atoms of oxygen, for instance, might have a considerable effect on their tendency to form oxonium salts. So far as we know there are no data sufficient to decide this question; but the fact that chloroanilic acid forms a quinhydrone easily[3] may indicate that the presence of two atoms of oxygen in the ortho position is favorable to the formation of these bodies, although in this case only one of them is quino oxygen. Here, then, may be another reason for the formation of the octohalogen orthoquinhydrones.

Torrey and Hunter[4] give reasons for believing that the green compounds obtained by them from tetrachloro- or tetrabromoquinone, whether para or ortho, and potassium or sodium iodide in acetone, are salts of octohalogen quinhydrones. If this view is correct, it is necessary to explain the formation of a salt of a quinhydrone, which cannot exist in the free state. They suppose it depends on the solubility, assuming that the octochloroquinhydrone is soluble, because Ling and Baker[5] found that the solubility of their quinhydrones increased with the amount of chlorine they contained. The soluble quinhydrone, therefore, would not

[1] Heinichen, *Ann.*, 253, 275 (1889).

[2] Hofman, *Ibid.*, 53, 47 (1845).

[3] Graebe, *Ibid.*, 146, 36.

[4] THIS JOURNAL, 34, 702 (1912).

[5] *J. Chem. Soc.*, 63, 1314 (1893).

be formed, while the nearly insoluble salt would be precipitated. Our observation that the octoiodoquinhydrone is nearly insoluble seems to us to remove the foundation of this hypothesis. We cannot, however, find one to replace it, unless, indeed, we guess that the presence of the sodium may reduce the negative effect of the eight chlorine atoms sufficiently to allow the formation of the oxonium salt.

Preparation of Iodoanil.

The bromoanil necessary for this work was prepared by a modification of Ling's method,[1] as follows: 50 grams of hydroquinone suspended in 300 cc. of glacial acetic acid were treated with 400 grams of bromine, followed by an excess of nitric acid of specific gravity, 1.42, and the mixture was heated gently. The product was pure enough to be converted directly into iodoanil.

The method for making the iodoanil differed in some particulars from that of Torrey and Hunter.[2] Twenty-five grams of bromoanil mixed with 23 grams of potassium iodide and 250 cc. of alcohol were heated on the steam bath under a reverse condenser for two hours. The reddish brown diiododibromoquinone obtained in this way, after being washed with water and alcohol, was returned to the flask and was heated again for two hours with 20 grams more of potassium iodide. The iodoanil formed was pure after two crystallizations from benzene, as shown by the following analyses:

0.2362 and 0.1927 g. subst. gave 0.3618 and 0.2965 g. AgI; calc. for $C_6I_4O_2$, 83.01% I; found, 82.80 and 83.18%.

The principal advantage of this method over that of Torrey and Hunter is the substitution of the much cheaper potassium iodide for sodium iodide in the second stage of the process, and the use of larger quantities of bromoanil. They found that poor yields were obtained with quantities larger than 15 grams, while with our modifications the process gave good results with as much as 50 grams, both as to quantity of yield and quality of product.

Octoiodoparabenzoquinhydrone.

Two grams of iodoanil (purified by one crystallization from benzene) were dissolved in 125 cc. of benzene, and after the addition of three drops of water the solution was completely saturated with sulfurous dioxide. It was then allowed to stand in a tightly corked flask at ordinary temperatures. At the end of three weeks there was no apparent change, the solution being still clear and dark red; but after the fourth week a considerable quantity of black shining crystals had been deposited, which were filtered out, washed several times with benzene, and dried *in vacuo*.

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[1] *J. Chem. Soc.*, **61**, 568 (1892).

[2] THIS JOURNAL, **34**, 708 (1912).

0.2864 g. subst. gave 0.4370 g. AgI; calc. for $C_6I_4O_2C_6I_4(OH)_2$, 82.86% I; found, 82.50%.

A parallel analysis confirmed this, but owing to an accident gave a still lower percentage.

Properties of Octoiodoparabenzoquinhydrone.—The substance was deposited from the benzene solution used in its preparation in narrow plates, or flat prisms, terminated often at both ends with two planes at an obtuse angle. Iodoanil, crystallized from benzene under similar conditions for the sake of comparison, appeared in similar long plates but narrower than those of the quinhydrone, and although one end was terminated by two planes at an obtuse angle, the other, when well developed, was bounded by a single plane at right angles to the sides. It was also harder to obtain large crystals from the iodoanil than from the quinhydrone. All these differences, however, while apparently constant, seemed to us more like differences in habit than in crystalline form. The quinhydrone is black with a metallic reflex and a brilliant luster, the iodoanil brown. In experiments similar to that described above, in which the moist benzene solution of iodoanil, after saturation with sulfurous dioxide, was allowed to evaporate slowly in an open flask instead of being tightly corked, some of the resulting crystals were brown and others black, although of the same size and thickness; and this difference was so marked that it could be used for distinguishing between the quinone and the quinhydrone.

The crystals of the octoiodoquinhydrone were permanent in the air, and when heated to 100° showed no loss in weight, or change of appearance. At 190° they began to decompose with evolution of violet vapors of iodine, and this decomposition continued, as the temperature rose, but the substance did not melt even at 265°. A parallel observation made at the same time showed that the iodoanil, from which the sample of quinhydrone was obtained, began to sinter at 260°, and was completely melted at 265°, the fusion being accompanied by decomposition but without evolution of iodine vapor.

The octoiodoquinhydrone is a very slightly soluble compound, being practically insoluble in alcohol, ether, chloroform, ethyl acetate, benzene, toluene, glacial acetic acid, or carbon disulfide, and slightly soluble in acetone, when the solvent is cold, but it is fairly soluble in any of these liquids if it is hot. In each case the solution was yellow, and the striking change from the black solid to the yellow solution suggested that the quinhydrone had dissociated. To study its behavior in this respect a quantity was dissolved with the aid of heat in toluene, and the solution allowed to evaporate spontaneously, when a residue was obtained consisting of brown flat needles of iodoanil mixed with white, amorphous tetraiodohydroquinone. Again a finely powdered crystal of the quinhydrone was treated with warm benzene, to which a little alcohol had been added. On evaporating the yellow solution the white tetraiodohydroquinone could be seen floating on the surface of the liquid, and the residue, as before, contained this white substance mixed with brown crystals of iodoanil. Iodoanil treated in exactly the same way showed only these brown crystals with no white admixture. A small amount of the quinhydrone was dissolved in glacial acetic acid, when, on adding sodium hydroxide cautiously, a white precipitate was obtained, which dissolved in the excess of the alkali, and was thrown down again by dilute sulfuric acid.

When a little of the quinhydrone was treated with twice normal sodium hydroxide the crystals were at once disintegrated, losing their crystalline form and yielding a brown powder, which we suppose to be iodoanil, and a yellow solution. This was poured off at once and acidified with dilute sulfuric acid, when a white precipitate was thrown down that redissolved in sodium hydroxide and is therefore probably tetraiodohydroquinone. A parallel experiment with iodoanil showed that it did not act at all with sodium hydroxide under the same conditions.

Determination of the Relative Solubilities of Iodoanil and Octoiodoquinhydrone.—A concentrated solution of iodoanil was made by dissoving it in benzene to which a few drops of water had been added. After the solution had stood at ordinary temperatures for a day with frequent shaking to guard against supersaturation, it was saturated with sulfurous dioxide and the flask, tightly corked, was placed in a bath at the constant temperature of 17°. When the solution had reached this temperature, 50 cc. were drawn out with a pipette, evaporated to dryness in a weighed watch glass, and weighed. The securely corked flask was weighed and replaced in the constant temperature bath. After standing for two weeks black crystals of the quinhydrone were deposited, and, as the weight of the flask was found to be unaltered, this crystallization was due to the formation of a less soluble compound, and not to evaporation of the solvent. A second portion of 50 cc. was now removed and the residue from it weighed, and the same treatment repeated at the end of two months. The results were as follows:

I. Weight of iodoanil in 50 cc. of benzene 0.5060 g. II. Weight of solid in 50 cc. benzene after standing two weeks with H_2SO_3, 0.4462 g.; weight of flask after I, 380.62 g.; weight of flask just before II, 380.52 g. III. Weight of solid in 50 cc. benzene after standing for two months with H_2SO_3, 0.3698 g.; weight of flask after II, and just before III, 335.2 g.

50 cc. of the solution therefore contained 0.1362 gram less solid after the formation of the quinhydrone than it contained before, showing that the quinhydrone is less soluble than the iodoanil.

Comparison of the Behavior of Iodoanil with that of Chloroanil and of Bromoanil.—One gram of each of the three substances was dissolved in

80 cc. of benzene containing 0.5 cc. of water. Each solution was saturated with sulfurous dioxide and allowed to stand at ordinary temperatures in loosely corked flasks (since these experiments were tried before we had found that the quinhydrone crystals were deposited without any evaporation of the solvent). After four weeks the flask containing the iodoanil showed crystals, some of which were black like the quinhydrone, others brown like iodoanil, but, as the black crystals were no larger than the others, the darker color could not be due to greater thickness. This black color, which we have never observed with iodoanil alone, justifies us in inferring that the quinhydrone had been formed, and we were confirmed in this belief by the peculiarities in habit of the two sorts of crystals, for, while the black were usually terminated at both ends by two planes at an obtuse angle, the brown showed only one such termination, the other, if well developed, consisting of a single plane at right angles to the sides. From the solution of chloroanil there had been deposited large clumps of white prisms evidently tetrachlorohydroquinone mixed with a small amount of yellow unchanged chloroanil, while only a yellow deposit of bromoanil was obtained from the experiment with this compound. Neither with chloroanil nor the bromoanil was there any indication of a substance with a darker color than yellow.

Action of Iodoanil on Tetraiodohydroquinone.—To determine whether the formation of the quinhydrone required that the hydroquinone should be in the nascent state, a mixture of iodoanil and tetraiodohydroquinone, in the proportion of two molecules of the former to one of the latter, was dissolved in warm benzene. Upon cooling brown crystals of iodoanil separated and the liquid was then allowed to stand in a loosely corked flask for several weeks, when the crystals deposited were found to consist of long, slender, brown prisms and broader, black, prismatic plates, from which we infer that octoiodoquinhydrone had been formed in this case also, although in smaller quantity than in the experiment, in which the iodoanil was reduced by sulfurous acid.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE SPLITTING OF BENZHYDROLS BY THE ACTION OF BROMINE.[1]

BY GUSTAVUS J. ESSELEN, JR. AND LATHAM CLARKE.

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In the course of a research on certain substituted benzophenones and benzhydrols, the authors observed that when bromine was allowed to

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, Cambridge, Mass., U. S. A., for the degree of Doctor of Philosophy by Gustavus J. Esselen, Jr.