red filtrate made slightly alkalin with potassium hydroxide. A small amount of dark precipitate separated and was removed. The filtrate was treated carefully with acetic anhydride, and a nearly colorless crystallin substance separated, soluble in excess of acetic anhydride. Recrystallized twice from water, after treatment with bone-black, and then twice from alcohol, it formed colorless needles, decomposing at about 270° (uncor.). Heated with concentrated potassium hydroxide solution, ammonia was evolved.

Calculated for $C_9H_9ON_3$: C, 61.68; H, 5.18; N, 24.00.
Found: C, 61.70; H, 4.53; N, 24.44, 24.57.

These results, although the hydrogen and nitrogen figures are rather wide of the mark, seem to indicate that the substance is the carbamidomethylbenzimidazole. It is soluble in hot water, in alcohol or glacial acetic acid; and difficultly soluble or insoluble in ether, chloroform or benzene.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE ACTION OF IODIDES ON BROMANIL. IODANIL AND SOME OF ITS DERIVATIVES.[1]

BY H. A. TORREY AND W. H. HUNTER.

Received March 18, 1912.

The work described in this paper was started with the intention of preparing some tetrahalogen derivatives of benzoquinone, having both bromine and iodine in the molecule, and studying the reactivity of the different halogens.[2] Data have been collected along two main lines: the study of the products of the reaction between potassium or sodium iodide and bromanil, and a preliminary study of the hitherto unknown iodanil. Use was made of both potassium and sodium iodide to effect the replacement of bromine by iodine, and both ethyl alcohol and acetone were used as solvents. Our use both of sodium iodide and of acetone was quite independent of the work of Finkelstein,[3] and as a matter of fact antedated its publication.

The addition of solid potassium iodide to a cold acetone solution of pure bromanil resulted in the setting free of iodine, and the formation of a green compound, which was rapidly destroyed if the solution was

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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 William Hammett Hunter.

This research was suggested by the late Professor H. A. Torrey, and the experimental work was carried on under his direction, but the writing of the paper was deprived of the benefit of his supervision by his too early death.—C. L. JACKSON.

[2] Prel. notice in *Ber.*, 38, 555 (1905).

[3] *Ber.*, 43, 1528 (1910).

heated. This green substance was due to an independent reaction and bore no relation to the bromoiodoquinones formed by heating the mixture, except that the reduction of a portion of the quinone removed it from the sphere of the subsequent action. When the mixture was heated, the principal product was brown, and melted at about 255–6°. It gave, on analysis, numbers corresponding closely with the theory for a dibromodiiodoquinone.

Further work after the publication of the preliminary notice showed that if large quantities were taken, the product had a much higher melting point. Crystallization experiments on an extended scale showed that this was not due to bromanil, which was absent. A fractionation led to three fractions, of melting points 276–282°, 255–259°, 256–61°. Analyses of these fractions showed that the first was composed of nearly pure tetraiodoquinone, the precipitate from the Carius determination showing on electrolysis in potassium cyanide that it was practically pure silver iodide. The second fraction was a mixture, probably of iodanil, dibromodiiodoquinone and bromotriiodoquinone, while the third fraction was almost pure dibromodiiodoquinone, showing that not only two, but all of the bromine atoms of bromanil could be replaced by iodine.

It was found that iodanil could be made the principal product of the reaction by heating first with potassium iodide, and next, with sodium iodide in alcohol. Prepared in this way, iodanil is a very dark brown substance, melting at 284–286° with evolution of iodine. Its color shows the strong deepening effect exerted by the replacement of chlorine or bromine by iodine. It crystallizes in needles, while chloranil and bromanil crystallize in thin plates, though dibromodiiodoquinone could be made to crystallize either in plates or needles.

A number of interesting derivatives of iodanil were prepared, for purposes of comparison with bromanil and chloranil. The reactions were chosen chiefly from some studied in the Harvard laboratory by Jackson and Grindley.[1]

As a result of the preparation of diiododiphenoxyquinone, and the diparacresoxy compounds from all three quinones, we were able to study the influence of the composition of these substances on their melting points, as shown in the following table.

	Diphenoxy.		Diparacresoxy.
Dichlor	243°	(Jackson and Grindley)	254–5°
Dibrom	266–7°	" "	262–3°
Diiod	290°		272–4° (sl. dec.)

In each case, the melting point of the bromine compound is almost exactly the mean of the melting points of the other two.

Other reactions studied were the formation of hemiacetals by sodium

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[1] *Proc. Am. Acad.*, 409 (1894).

alcoholates on the quinone, which also led to the formation of the very interesting iodoanilic acid, and the action of aniline on the diiododiphenoxy quinone. In the latter case we found not only a replacement of phenoxy by anilino groups, but of iodine by hydrogen as well, giving dianilinoquinone and the monoanil of monoiododianilinoquinone. This result was not unexpected, as we had already found that aniline on dibromodiiodoquinone gave us dianilinoquinone and probably monobromodianilinoquinone. This is a case of the replacement of halogen by hydrogen in benzene derivatives, a reaction being studied by Professor Jackson, who has previously found many instances of it, some of which are noted in the introduction to his paper with Grindley.

The study of the derivatives of iodanil has been continued in this laboratory, and a considerable quantity of material is now ready for publication.

Although bromotriiodoquinone was isolated from iodanil mother liquors, it is so difficult to obtain in quantity in a pure state that little work could be done on it. It crystallizes in short, brown, prismatic needles, melting at 253–4°. It gives, with sodium phenolate, monobromomonoiododiphenoxyquinone, of melting point 282–283°, which is identical with the compound obtained before from dibromodiiodoquinone and described as melting at 281–282°.

The formation of the same bromoiodoquinone from these two quinones is certainly unexpected, if the phenoxy groups always enter in the 2,5-position, as has been supposed, because it would certainly be expected that the iodine atoms in dibromodiiodoquinone would be in the 2,5-position also. The most probable explanation is that in the early part of the work, while trying to make some of the diiodo compound, we actually hit on the triiodo compound instead. This might easily have happened, as at that time it was not known that more than two atoms of bromine could be removed from bromanil by potassium iodide, and the melting point of the triiodo compound is so close to the melting point of dibromodiiodoquinone, that it would have been impossible to distinguish the two by this single property. If this is not the explanation, we are forced to believe that the replacement of bromine by iodine takes place on differently placed ring atoms than that of halogen by the phenoxy groups, or that the iodine atoms are not para to each other in dibromodiiodoquinone. Either of these suppositions is out of harmony with our knowledge of quinones up to the present time, so it seemed important to us to prepare a diphenoxy derivative from undoubted dibromodiiodoquinone. The preparation of this compound in a pure state unfortunately succeeded only at the close of our work together, and as a result we are unable to make any final statement in regard to the action of sodium phenolate on dibromodiiodoquinone.

Dibromodiiodoquinone is obtained as a light brown compound, crystallizing in needles if slowly cooled but in plates if cooled rapidly. It melts at 258–259° in a pure state, instead of at 255–256°, as given in the preliminary notice.

The replacement of bromine by iodine is not the only effect of potassium iodide on bromanil. It has already been mentioned that on mixing the solid, finely ground potassium iodide with the bromanil in acetone, a green substance was formed, if the solution was cold. Chloranil gave an identical action, and sodium iodide in acetone readily gave precipitates with chloranil, bromanil, tetrabromo-*o*-quinone, and tetrachloro-*o*-quinone. The potassium derivative from chloranil and the sodium derivatives from chloranil and tetrabromo-*o*-quinone were analyzed, and indicated that they were the alkali salts of the unknown octohalogen quinhydrones. This result was confirmed by the action of dilute sulfuric acid on the sodium salt from chloranil, which gave chloranil and tetrachlorohydroquinone. We actually had, therefore, salts analogous to those of known quinhydrones described by Jackson and Oenslager.[1]

The question as to why the salts of these quinhydrones should be stable, when the free quinhydrones are unknown, is an interesting one. Ling and Baker[2] found that they could get a hexachloroquinhydrone, but not an octochloro compound, and decided that the stability is in inverse proportion to the number of halogen atoms, but that this cannot be the only condition influencing stability is shown by the existence of our salts. Hardenbergh[3] and one of us found that quinhydrone and phenoquinone are dissociated in solution in accordance with the reversible equation

$$C_6H_4O_2 + C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2.C_6H_4(OH)_2.$$

Ling and Baker point out that the lower halogenated quinhydrones are insoluble in cold alcohol, while the higher members are soluble. It would seem, then, that the question of the formation or non-formation of a given quinhydrone may be a function of the solubility of its factors and of the compound itself. Just as Hardenbergh and one of us were able to throw out quinhydrone[4] from solutions by addition of either factor, so addition of a great excess of a factor might throw out a quinhydrone which did not precipitate on the usual mixing of equal molecules. The octochloroquinhydrone should be fairly soluble, while chloranil and tetrachlorohydroquinone are not very soluble, and this is probably why Ling and Baker could not obtain the quinhydrone. So the stability of

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[1] *Am. Chem. J.*, **18**, 4 (1896).

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

[3] *Am. Chem. J.*, **33**, 167 (1905).

[4] *Loc. cit.*

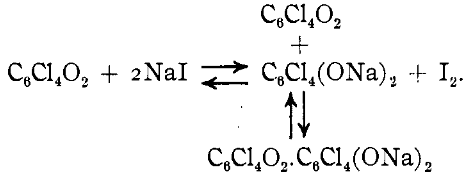
the halogenated quinhydrones may be considered to depend on the number of halogens present only as this affects the solubility of the factors and of the quinhydrone itself.

For instance, in the present case, the green salt is so insoluble that the solutions of chloranil and iodide need only be mixed to cause the precipitation, but a far greater yield is obtained with the more soluble sodium iodide than with potassium iodide.

The relation between the reduction reaction and the substitution reaction is also interesting. The reduction reaction, best shown by chloranil, is a balanced one:

$$C_6Cl_4O_2 + 2NaI \rightleftharpoons C_6Cl_4(ONa)_2 + I_2$$

At low temperatures, the equilibrium is far to the right, on account of the precipitation of green salt, but at high temperatures the dissociation of the quinhydrone salt and the oxidizing effect of the iodine increase together, driving it back to the quinone, which then reacts with the sodium iodide to substitute iodine for chlorine or bromine. A complete picture of the equilibria in the reduction is then given by the scheme



$$\begin{array}{c} C_6Cl_4O_2 \\ + \\ C_6Cl_4O_2 + 2NaI \rightleftharpoons C_6Cl_4(ONa)_2 + I_2. \\ \uparrow\downarrow \\ C_6Cl_4O_2.C_6Cl_4(ONa)_2 \end{array}$$

That the reactions are independent is shown by two facts. Cold, 95% alcohol as solvent does not lead to the formation of green salt, but on standing months, gives the substitution reaction. This shows the effect of non-formation of green salt in allowing the other reaction to occur. The other point showing the independence of the reactions is that in a regular preparation of iodoquinones, the iodine set free accounted for all the bromanil which did not appear as iodoquinones, showing that the formation of the iodoquinones is not connected with the formation of green salt, which is a secondary reaction, in consequence of the reduction of part of the quinone.

Experimental Part.

Bromanil was prepared by a modification of the method of Ling:[1] 20 grams of hydroquinone were suspended in glacial acetic acid, and 175 grams of bromine (6 mol.) were added. After standing over night, an equal volume of water and some concentrated nitric acid were added and the mixture heated on the steam bath till bromine was no longer evolved. The nitric acid liberates bromine from the hydrobromic acid present, and a more complete bromination occurs. The bromanil

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

was crystallized from glacial acetic acid, and a product melting at 290° or over was used for our work. Pure bromanil melts at 300°[1] and it was shown by analysis that about 2.5% of tribromoquinone lowered the melting point about 25°.

Action of Potassium Bromide in Hot Alcohol on Bromanil.—Twenty grams of bromanil were heated two hours with 20 grams finely ground potassium iodide in alcohol, under a reflux condenser. The product was fractionated, using ethyl acetate as solvent. Three fractions resulted, of the following melting points and composition:

(A) Most insoluble. Melting point, 276–282°.

Calculated for $C_6I_4O_2$: I, 83.00. Found: 83.90, 83.78.

The precipitate from the second analysis on electrolysis gave: Ag = 46.08%. AgI requires 45.95% Ag.

(B) Melting point, 254–6°. Calculated precipitate as AgBrAgI.

Calculated for $C_6Br_2I_2O_2$: Br + I = 79.92. Found: 78.65, 78.13.

Calculated precipitate as $AgBr_3AgI$.

Calculated for $C_6BrI_3O_2$: Br + I = 81.58. Found: 83.00, 82.55.

(C) Most soluble fraction. Melting point, 255–9°.

Calculated for $C_6Br_2I_2O_2$: Br + I = 79.92. Found: 80.23, 80.24.

From these data it is obvious that instead of dibromodiiodoquinone only, as stated in the preliminary paper, potassium bromide gives with bromanil bromotriiodoquinone and iodanil as well. Methods were found for isolation of all three, as follows:

Dibromodiiodoquinone.—This was found to be the principal product, in the following conditions:

Ten grams of bromanil and 7.8 grams of potassium iodide (2 mol.) were heated two hours under a reflux condenser with 100 cc. of alcohol. The reaction mixture was then poured into water, filtered, and the brown precipitate washed with water and alcohol. Careful crystallization from ethyl acetate gave a substance of melting point constant at 258–59°, with slight sublimation. Analyzed for halogen.

Calculated for $C_6Br_2I_2O_2$: Br + I= 79.92.[2] Found: 80.49.

This checks with the results in the preliminary notice; found: 79.79, 79.76.

One of these precipitates had been analyzed for silver by the method of Mansel,[3] solution in thiosulfate, and precipitation by ammonium sulfide.

Calculated for AgBrAgI: Ag, 51.30. Found: 51.09.

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[1] Graebe and Weltner, *Ann.*, **263**, 33 (1891).

[2] Calculations of these analyses were made by separate calculations for each possible ratio of bromine and iodine. This led to better results than the "indirect" method, which led in the case mentioned above to wide variations from the theoretical, though the silver determination checks the composition fairly closely.

[3] *Z. anal. Chem.*, **9**, 208 (1870).

Analysis for carbon and hydrogen. Silver spirals and "molecular" silver were necessary to hold back iodine.

Calculated for $C_6Br_2I_2O_2$: C, 13.91; H, 0.0.
Found: (I) C, 13.95; H, 0.15.
(II) C, 14.25; H, 0.30.

Dibromodiiodoquinone is a reddish brown substance, melting at 258–9°. It crystallizes from ethyl acetate in plates on rapid cooling, and in deep red brown prismatic needles on cooling slowly. It is more soluble than iodanil, but less than bromanil, in all other solvents. It is soluble in ethyl acetate, benzene, acetone, glacial acetic acid, less soluble in alcohol, chloroform, ether, and ligroin. Reduction by sulfur dioxide in acetone and water gave a colorless substance, melting, crude, at 243–244°. The quinone is unaffected by acids, but readily decomposed by alkalies.

Bromotriiodoquinone.—In the mother liquors from the preparation of iodanil, there was obtained a quinone of constant melting point 253–254°, which was at first supposed to be dibromotriiodoquinone. It proved, on analysis, to be bromotriiodoquinone. $C_6BrI_3O_2$ requires $Br + I = 81.58\%$. Found: 81.44, 81.24.

It crystallizes in rather short, broad, prismatic crystals, rich brown in color, intermediate in solubilities between iodanil and dibromodiiodoquinone. It melts within less than a degree. Sodium phenylate reacts with it to form bromoiododiphenoxyquinone.

Iodanil.—Fifteen grams of powdered bromanil were treated with 11.7 grams (2 mol.) of potassium iodide in 150 cc. of alcohol. The yield was poor if larger amounts were used. The mixture was heated two hours on the steam bath with a reflux condenser, and cooled rapidly, filtered with suction, and the red brown substance filtered with suction and washed with alcohol and water. It was then replaced in the flask with 10.6 grams (2 mol.) of sodium iodide and 150 cc. of alcohol, and heated two hours more. The substance rapidly became dark brown. It was isolated by filtration and washing free of iodine, and recrystallized from ethyl acetate till it showed the constant melting point 282–284°. It is a slow process to raise the melting point above 270°, apparently because of formation of mixed crystals. Sodium iodide must be used in the second part of the heating, as potassium iodide leads to the formation of a purple compound containing potassium, which is not further acted on.

Iodanil crystallizes in small chocolate colored needles, melting at 282–284° with evolution of iodine. It is slightly soluble in benzene, glacial acetic acid, acetone and cold ethyl acetate, fairly soluble in hot ethyl acetate; practically insoluble in the other common solvents. Acids have no action, but alkalies evidently produce a deep seated change.

Derivatives of Dibromodiiodoquinone.

Action of Amines.—An addition product with diphenylamine of the type studied in this laboratory by Jackson and Clarke[1] was prepared as follows: A large excess of diphenylamine was dissolved in ligroin and powdered dibromodiiodoquinone, which is only slightly soluble in ligroin, was allowed to stand in this solution until it had all become converted into the fine purplish black needle-like crystals of the addition product, which was filtered off and washed with a little ligroin. It resembled in every way the compounds described by Jackson and Clarke, and so proved the quinone nature of our compound. It melted over a wide range of temperatures, according to the speed of heating, and was decomposed by most solvents, leaving the quinone. The dry substance gave a green powder on grinding. It was placed in a desiccator over hard paraffin until analyzed.

Calculated for $C_6Br_2I_2O_2.(C_6H_5)_2NH$: Br + I = 60.23. Found: 60.31.

Action of Potassium Phenolate.—Bromoiododiphenoxyquinone was prepared by treating 1.5 grams of the powdered dibromodiiodo quinone with a solution of 0.3 gram caustic potash and 0.6 gram phenol (= 2 mol. potassium phenolate), and heating two hours on the steam bath with a reflux condenser. A salmon colored substance resulted, which was filtered off, and washed well with water. Both bromine and iodine salts were found in the filtrate. It was crystallized from toluene till it showed a constant melting point, 281–282°. (This melting point was raised to 282–283° when the substance was prepared from bromotriiodoquinone.) In the mother liquors was found a small amount of a red substance, melting at 227–231° after two crystallizations, which was probably the tetraphenoxyquinone described by Jackson and Grindley, who give the melting point as 229–230°. The diphenoxy compound was analyzed for halogen.

Calculated for $C_6BrI(OC_6H_5)_2O_2$: Br + I = 41.62. Found: 41.62, 42.16.

The substance was shown to contain both bromine and iodine by decomposition with strong caustic soda, and application of the usual tests. It melts at 282–283°, with sintering just before melting. It is soluble in ethyl acetate, benzene, and toluene, the last being an excellent crystallizing medium for it. It is somewhat soluble in alcohol, ether, and acetone, almost insoluble in ligroin. Acids are without effect, but alkalies decompose it, first splitting off the phenoxy groups.

Action of Aniline.—Some dibromodiiodoquinone was dissolved in toluene, a large excess of aniline added, and the mixture boiled for an hour under a reflux condenser. The solution turned brown, a thick precipitate appeared and, on cooling, the liquid almost solidified. Crystallization from toluene separated the precipitate formed into two compounds,

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[1] *Am. Chem. J.*, **34**, 441 (1905).

a plum colored and a yellow substance. The plum colored compound is almost insoluble in toluene and was identified as dianilinoquinone by crystallization from hot nitrobenzene, analysis, and by comparison with a known sample, made by the method of A. W. Hofmann.[1]

Calculated for $C_6H_2(NHC_6H_5)_2O_2$: N, 9.66. Found: 9.28, 9.37.

The yellow compound crystallized from toluene abundantly, in the form of fine yellow needles. It was recrystallized several times, but as it did not melt at 300°, it was hard to decide as to its purity. Three different samples gave varying halogen contents, and but one nitrogen determination had been made when it became necessary to end the work.

Calculated for $C_6HBr(NHC_6H_5)_2O_2$:	Br, 21.66; N, 7.61.
Found:	Br, 19.18, 23.90, 21.89; N, 7.69.

There was no iodine in the precipitate from the first halogen analysis. It seems safe, therefore, to consider that the substance formed was bromodianilinoquinone.

The Action of Potassium Phenolate on Bromotriiodoquinone.—One and one-half grams of pure substance were heated an hour and a quarter with a solution of two molecules of potassium phenylate. The diphenoxy compound resulting was then filtered, washed, and crystallized from toluene, when it showed the constant melting point 282–283°, hence, was the bromoiododiphenoxyquinone described before, as the dibrom compound melts at 266–267°, and the diiodo compound at 290°.

Derivatives of Iodanil.

Action of Phenolates.—Two and one-half grams of iodanil were treated with a little over two molecules of sodium phenolate, dissolved in 25–30 cc. of water, and the mixture heated an hour on the steam bath. The salmon colored precipitate formed was washed with water, then with alcohol, and dried. After crystallization from toluene it reached the constant melting point 290°.

Calculated for $C_6I_2(OC_6H_5)_2O_2$: I, 46.67. Found: 46.42.

The precipitate gave a negligible extract on three days' treatment with strong ammonia.

The diiododiphenoxyquinone resembles the other diphenoxy compounds in color and solubilities. It differs in its reactivity to sodium hydroxide, as it does not give iodanilic acid on warming, but instead, ether extracts from the filtered and acidified solution give a yellow compound, which may, perhaps, be the mono ether. It was not investigated.

The Action of Cresolates.—It was thought worth while to try the action of the different cresolates on iodanil, and their action was tried on bromanil and chloranil also. *o*-Cresolates were found to give much black tar; the *m* compounds were more like the phenolates, though a compound was isolated only from bromanil. The *p*-cresolate worked

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[1] *Jsb.* (1863), 413.

very smoothly, in the same manner as the phenolate. The cause of the difference may be that the methyl groups are attacked in some way by the quinone, leading to the formation of the tarry products. The method used was identical with that for the phenolates, save that where tar was formed, it was removed with alcohol, in which the cresoxy compounds are not very soluble.

Dibromodi-m-cresoxyquinone.—Fine, salmon red needles from benzene-ligroin. Melting point constant at 193°.

Calculated for $C_6Br_2(OC_6H_4OCH_3)_2O_2$: Br, 33.46. Found: 33.8.

Much more soluble in all solvents than the diphenoxy compounds.

Dibromodi-p-cresoxyquinone.—Salmon colored needles from toluene, melting at 254° with decomposition on slow heating, at 262–263° with decomposition on rapid heating.

Calculated: Br, 33.46. Found: 33.07.

Dichlorodi-p-cresoxyquinone.—It was necessary here to moisten the chloranil with dilute acetone before adding the cresolate solution, which was made up with 1 : 2 caustic potash, and only five minutes' heating was necessary. Melting point from toluene, 254–5°, with rapid heating.

Calculated for $C_6Cl_2(OC_6H_4CH_3)_2O_2$: Cl, 18.11. Found: 18.23.

Diiododiparacresoxyquinone.—Heated one hour, concentrated cresolate solution. Melting point became constant at 272–274°, with blackening at 269°, and evolution of iodine.

Calculated: I, 44.38. Found: 44.89.

Sodium Alcoholates on Diiododiphenoxyquinone, Diiododiethoxyquinonediethylhemiacetal.—One and four-tenths grams of diiododiphenoxyquinone were treated with a little over four atoms of sodium dissolved in 20 cc. of absolute alcohol. The reaction started immediately, and was allowed to continue with stirring and breaking up of the diphenoxy compound, until all the red color of the latter had disappeared. There was then present a white precipitate of the sodium salt of the hemiacetal, as was found by Jackson and Grindley in their work.[1] This was not isolated, but dissolved by adding the requisit water. The filtered solution was then acidified with dilute sulfuric acid and the white granular precipitate of the hemiacetal was filtered, washed well with water till the wash-waters were colorless, then dissolved in dilute caustic soda and reprecipitated, filtered and washed. This alternate precipitation and solution was continued until the precipitate collected was white. Much iodanilic acid was formed from the hemiacetal during this purification, as was shown by the purple color of the solutions and wash waters, and a considerable amount of it was recovered from the wash waters. The hemiacetal was pure white, as viewed in the clear liquid, but when collected,

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[1] *Proc. Am. Acad.*, **29**, 432 (1894).

it was faintly yellow. It was air dried, brought to constant weight *in vacuo*, and analyzed.

Calculated for $C_6I_2(OC_2H_5)_2(OH,OC_2H_5)_2$: I, 47.01. Found: 46.81 per cent.

It was possible to obtain this hemiacetal in minute crystals by evaporation of its solutions. No other member of the class has been obtained in crystallin form. It is somewhat soluble in cold alcohol, less in the other ordinary solvents. It forms a red compound, presumably diiododiethoxyquinone, on heating with hydrochloric acid on the steam bath, and also on heating the dry hemiacetal in a melting point tube to 140°.

Diiododimethoxyquinonedimethylhemiacetal.—One and one-half grams of diiododiphenoxyquinone were treated with a little over four atoms of sodium, dissolved in 25 cc. of absolute methyl alcohol. No sodium salt was precipitated. The purification was identical with that of the ethyl compound.

Calculated for $C_6I_2(OCH_3)_2(OH, OCH_3)_2$: I, 52.45. Found: 52.46.

This hemiacetal was almost pure white. It was somewhat soluble in all the ordinary solvents, but did not crystallize. It lost two molecules of alcohol under the same conditions as did the ethyl derivative. It was found that the sodium salt could be made from iodanil as easily as from diiododiphenoxyquinone, by the direct action of sodium methylate.

Iodanilic Acid.—This could not be formed as the corresponding chlorine and bromine compounds by the direct action of alkalies on the quinone or on the diphenoxy derivative. Three grams of crude iodanil were treated with an excess of sodium methylate solution. The quinone dissolved. The hemiacetal was isolated as before, and dissolved in considerable *N* caustic soda. This solution was heated till it just commenced to boil when it turned the color so characteristic of the alkali salts of the "anilic" acids. It was allowed to cool, and the perfectly clear solution was acidified with dilute sulfuric acid, causing a copious precipitate of iodanilic acid. About one or two cc. of concentrated sulfuric acid were then added to complete the precipitation, whereupon the solution turned yellow in a very characteristic manner. The filtered precipitate was washed till the wash water commenced to run through purple, showing the almost complete absence of sulfuric acid. Nine-tenths gram of air-dried acid was obtained. It was purified by crystallization from benzene, whence it was deposited in hard transparent red needle-like crystals, becoming opaque in the air. Dried at 100°.

Calculated for $C_6I_2(OH)_2O_2$: I, 64.78. Found: 65.04.

Part of the crude acid was less soluble in benzene, and proved to be a yellow compound, slightly soluble in water, readily in alkalies. It was, perhaps, the hemiether of iodanilic acid, for it resembled the yellow substance obtained as one product of the action of alkali on diiododiphenoxyquinone. It is hoped that the study of these compounds will be continued in this laboratory.

Properties of Iodanilic Acid.—It dissolves in water with the same purple color as chloranilic and bromanilic acids. Strong sulfuric acid precipitates it from concentrated aqueous solution in yellow red feathery crystals, while dilute acids throw down a reddish precipitate. The two precipitates probably differ in content of water, as the chloranilic and bromanilic acids precipitate in hydrated form. Iodanilic acid dissolves in benzene with a yellow red color, presumably corresponding to the anhydrous state. It commences to decompose at about 205°, giving off iodine.

The Action of Aniline on Diiododiphenoxyquinone.—Two grams of the diphenoxy compound were warmed on the steam bath with 10 cc. of aniline for a few minutes, when the color of the diphenoxy compound disappeared. The mixture was cooled and freed from aniline by dilute sulfuric acid, when the gray brown amorphous mass was washed with water till the acid reaction disappeared from the wash waters. The product was then dried and treated with hot toluene. This separated it into two compounds, a purple and a yellow substance.

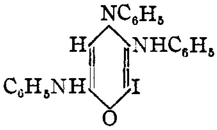
I. *Dianilinoquinone.*—The part almost insoluble in hot toluene was expected to be dianilinoquinone, after our experience with the dibromodiiodoquinone, so it was dissolved in hot nitrobenzene and filtered with suction. We obtained partly on the filter and partly in the filtrate the familiar purple plates of dianilinoquinone. The substance on the filter seemed a little brighter, so it was washed well with alcohol, dried, and analyzed for nitrogen.

Calculated for $C_6H_2(NHC_6H_5)_2O_2$: N, 9.65. Found: 9.91.

It gave with sulfuric acid the same red purple color shown by a known sample.

II. *The Yellow Compound.*—This was crystallized from boiling alcohol, each time a very small amount of a brownish substance, insoluble in cold alcohol, being left undissolved, although all the material present had been in clear solution in the alcoholic filtrate just before cooling. After several crystallizations, it was dried and analyzed.

Calculated for



: I, 25.84. Found: 25.61.

This analysis showed that by using undiluted aniline on the diphenoxy compound, instead of the toluene solution used in the case of the dibromodiiodoquinone, a monoanil had been formed instead of the expected monoiododianilinoquinone. As the time at our disposal did not allow of the manufacture of another sample for a determination of carbon and hydrogen, the following experiment was performed as a check. A little of the substance was boiled about three minutes with dilute hydrochloric acid, as this reagent has no effect on anilino groups, but decomposes anils, setting free aniline. The solution was filtered, and from the filtrate was obtained the isonitrile reaction, which was regarded as proof of the presence of aniline, and hence of an anil grouping in the original substance. In this connection also is to be noted the formation of an insoluble substance in small amount on each boiling of the compound with alcohol. This was presumably due to the splitting off of the anil grouping by boiling with alcohol, giving the monoiododianilinoquinone, which would probably be insoluble in cold alcohol, as was the corresponding bromine derivative.

The monoiododianilinoquinonemonoanil crystallizes from alcohol in fine dark needles, a deep yellow brown, usually grouped in clusters. It decomposes at about 225°, with fumes of iodine, and the resulting residue is not melted at 300°. Readily soluble in chloroform or hot alcohol, only slightly in acetone or cold alcohol, almost insoluble in ether or ligroin. It gives a full purple with strong sulfuric acid.

The Action of Cold Iodides on the Tetrahalogen Quinones.

Chloranil and Potassium Iodide.—To a saturated solution of pure chloranil in dry cold acetone was added solid potassium iodide in the form of good sized crystals, when the green precipitate appeared immediately, accompanied by the color of free iodine, the presence of which was readily shown by the starch test. After a short time the solution was gently shaken, and the liquid with the light precipitate suspended was poured off upon a Büchner funnel, when, after washing with more acetone and allowing it to dry, it was found to be grass green, and under the microscope it showed needles. It was realized that the addition of solid potassium iodide was undesirable, but it was considered unavoidable, as mixing the saturated solutions gave only a minimum precipitate, and the analyses show that by the method of floating the light precipitate away from the heavy potassium iodide, a clean separation is really effected, The precipitate was dried *in vacuo*.

Calculated for $C_6Cl_4O_2.C_6Cl_4(OK)_2$: Cl, 49.74; K, 13.74.
Found: Cl, 49.36; K, 13.62.

The salt forms grass green needles, which dissolve in acetone to a brownish solution; it is slightly soluble in ethyl acetate, benzene, or toluene. On heating, it does not melt, but gives off a yellow sublimate, probably chloranil, and leaves a black residue. It dissolves in dilute caustic potash to form a green solution, which decomposes on warming. Pure water hydrolyzes the compound fairly rapidly, and when allowed to stand with it a long while, it gradually becomes converted into a white amorphous compound, containing no potassium. This was filtered, washed and dried. Two different specimens were analyzed for chlorine, giving numbers close to the theory for a hemiether, but no further work was done on this substance.

Calculated for $C_6Cl_4(OH)$-*o*-$C_6Cl_3O_2$: Cl, 54.29. Found: 54.10, 54.48.

Chloranil and Sodium Iodide.—This iodide, being readily soluble in acetone, gives the green salt readily on mixing saturated solutions of the two compounds. Care was necessary that the acetone solutions should be dry and distinctly cold to the touch. The copious precipitate was filtered with suction, washed with acetone, and dried *in vacuo* for analysis.

Calculated for $C_6Cl_4O_2.C_6Cl_4(ONa)_2$: Na, 8.43. Found: 8.57.

The salt is blue green. Otherwise it corresponds in properties to the potassium compound. Dilute sulfuric acid gave a whitish precipitate, which was extracted with alcohol. From the alcohol were obtained long needles, melting at 231–233°, without recrystallization, therefore, tetrachlorohydroquinone, the melting point of which is 234°. It was readily oxidized by nitric acid to chloranil, shown by crystallization from acetone in the characteristic lemon yellow plates, which sublimed without decomposition, and melted in a closed tube at 280–282°, chloranil melting under those conditions at 290°. There were also obtained from the portion insoluble in the alcohol, by crystallization from acetone, crystals of chloranil, melting at 285–286°. Sulfuric acid, therefore, decomposes the salt into a mixture of chloranil and tetrachlorohydroquinone.

Tetrabromo-o-quinone and Sodium Iodide.—Two grams of the quinone dissolved in 15 cc. of dry acetone and 2 grams of sodium iodide dissolved in 30 cc. were mixed together, after filtering, by pouring the quinone solution into the iodide solution. The flask was then rinsed into the iodide solution with 10 cc. more of dry acetone, and the mixture shaken vigorously. The reaction was instantaneous, and the precipitate, black while wet, was filtered off with suction, washed well with acetone and finally with ether, as preliminary experiments had shown that acetone reacted with the salt on long standing. It was then well pressed out and placed in a vacuum desiccator over night. In the morning the corners of the mass had become very slightly tarry, so they were cut off, and the rest of the green salt, which was unaltered, was brought to constant weight over calcium chloride for analysis.

Calculated for $C_6Br_4O_2.C_6Br_4(ONa)_2$: Br, 71.57; Na, 5.16.
Calculated for $C_6Br_4O_2.C_6Br_4(ONa)_2.{}^1/_2CH_3COCH_3$: Br, 69.32; Na, 4.99.
Found: Br, 68.95; Na, 5.00.

The salt precipitates in bluish green needles, about the color of the salt from chloranil. It is much less stable than the other salts analyzed, decomposing on heating to 80° for a short while, probably on account of the presence of the acetone.

Like precipitates were readily obtained from bromanil and tetrachloro-*o*-quinone.

Estimation of Iodine Set Free.—For the purpose of determining the amount of free iodine formed in the reaction of iodides with bromanil, 10 grams of the powdered crystals, melting at 292–293°, were boiled two hours with 10 grams of potassium iodide in alcohol. The solution was then filtered, the precipitate washed with alcohol till no more iodine color was visible in the alcohol used for washing, and the alcohol filtrate and washings made up to 250 cc. This solution was then titrated for iodine with a thiosulfate solution, 1 cc. of which was equivalent to 0.01 gram of iodine. Much difficulty was found in estimating the end-point, as the reduction products of the quinones present darkened the liquid considerably, and obscured the blue color, so it seemed best to use but 10–15 cc. and titrate rapidly. In nine titrations, the following values were found for 1 cc. of the thiosulfate solution in terms of the iodine solution: 2.20, 2.23, 2.19, 1.19, 1.88, 2.17, 2.29, 2.34, 2.36. The average of these is 2.16, which corresponds to 1.1 grams of free iodine in solution as reaction product. The insoluble quinones from the reaction weighed 9.6 grams and melted at 253–258°. Calculated as dibromodiiodoquinone, it is equivalent to 7.9 grams bromanil, but as a matter of fact it is equivalent to less bromanil, as it was not all dibromodiiodoquinone. This corresponds roughly, then, to the disappearance as various reduction products of 2.1 grams bromanil. The 1.1 grams of iodine formed would be set free by 2.0 grams of bromanil, showing that the iodine formed, as was to be expected, really does come from reduction of the bromanil which does not appear as iodo derivative.

Potassium Iodide in Cold Alcohol on Bromanil.—Ten grams of pure bromanil, 10 grams potassium iodide and 100 cc. of alcohol were placed in an Erlenmeyer flask, closed with a rubber stopper, and allowed to stand with no heating, and with only occasional shaking, for four months. No green salt was visible at any time. The final substance in the flask was red brown; isolated as usual, it melted at 242–245°, and on crystallization from ethyl acetate, showed that the effect had been in no wise different from that produced when heated.

THE AMYGDALINS AND THEIR INTER-REACTIONS WITH EMULSIN.

By Vernon K. Krieble.

Received March 11, 1912.

In a previous communication[1] from this laboratory, it was proved that the rotation of a racemized amygdalin solution is independent of the nature and of the concentration of the alkali and that the equilibrium point is independent of the temperature and of the concentration of the

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[1] Walker and Krieble, *J. Chem. Soc.*, 95, 1437.