

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

ON THE ACTION OF SODIUM HYDROXIDE ON IODOANIL.¹

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A study of the literature has shown that, when chloroanil or bromoanil is treated with an alkaline hydroxide, the product is chloroanilic acid, or bromoanilic acid² with a single exception observed by Kehrmann,³ who, while obtaining chloroanilic acid with alcoholic potassium hydroxide in the cold, found that when hot the product was metadiethoxydichloroquinone. Experiments of our own also with bromoanil led in every case to bromoanilic acid; but Torrey and Hunter⁴ observed that, when iodoanil was treated with alkalis, the product frequently was not iodoanilic acid; and this difference in the behavior of chloroanil and bromoanil, on the one hand, and iodoanil, on the other, is so interesting that we have studied it in detail in our continuation of their work.

The products obtained by the action of alkalis on iodoanil differ according to the conditions of the reaction. By the action of sodium hydroxide on iodoanil, suspended in a mixture of 30 cc. of water and 15 cc. of alcohol, a sodium salt is formed, which looks like sodium iodoanilate, and, like it, crystallizes with water in dark purple prisms terminated at each end by two planes at an obtuse angle, leaving, however, when dried a purplish black residue instead of the brownish purple anhydrous sodium iodoanilate. On acidification a substance is precipitated, which crystallizes from hot toluene in red needles, in the cold in rhombic plates containing toluene of crystallization. This might be a description of iodoanilic acid, and, although a careful comparison reveals slight differences, such as a tendency to spindle forms in the needles, and truncation of the obtuse angles of the plates, neither of which appear in iodoanilic acid, these are rather differences in habit, such as might be caused by the presence of an impurity, than real differences in crystalline form. In view of these marked similarities very convincing arguments are necessary to show that we have a new substance and not somewhat impure iodoanilic acid, especially as most various reagents convert it into iodoanilic acid or some of its derivatives.

Our reasons for believing it to be a new compound are the following: (1) The new product contains about one and a half per cent. more iodine than iodoanilic acid, and, as six agreeing analyses were obtained from six different preparations crystallized from one to four times from toluene,

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 Stenhouse, *J. Chem. Soc.*, 8, 6 (1870); Graebe, *Ann.*, 263, 16 (1891).

³ *J. prakt. Chem.*, 39, 318 (1889).

⁴ *THIS JOURNAL*, 34, 702 (1912).

it can hardly be that the excess of iodine was due to an impurity. (2) We next tested for an impurity, and, as this must raise the percentage of iodine, the only probable ones were sodium iodide and iodoanil. A specimen of our salt, therefore, was decomposed with enough dilute sulfuric acid to precipitate most of the organic matter, and the filtrate tested for an iodide, when it gave a trace of a red precipitate (probably only silver iodoanilate) but, even if it were in part silver iodide, the amount was very far from enough to account for the difference in the percentages. As the precipitate with sulfuric acid dissolved completely in water, no iodoanil could be present. This solution was then boiled for a few minutes, which converts the substance completely into iodoanilic acid, and after precipitating this with an excess of dilute sulfuric acid the test for iodide was repeated with the same negative result as before. No sodium iodide or iodoanil, therefore, was present.

(3) This last experiment seems to us to give a conclusive proof of the nature of the compound, for starting with a substance containing 66.50% of iodine we have converted it by boiling with water into iodoanilic acid, which contains only 64.78%, and this lowering of the amount of iodine has been accompanied by no setting free of any compound containing iodine. The only explanation we can find for these observations is that the substance is the hemiether of iodoanilic acid, I, $[C_6I_2(OH)O_2]_2O$, and by taking up one molecule of water it is converted into iodoanilic acid with its smaller percentage of iodine. Such a hemiether might well show a marked resemblance to the acid with only slight differences as described above, and would undergo the change to the acid with a great variety of reagents.

(4) The salt to be expected from the hemiether $[C_6I_2(ONa)O_2]_2O$ would contain 5.68% of sodium, the sodium iodoanilate 10.55%, so that it seemed analyses of this sodium salt would settle the question. The material used for analysis was made direct from iodoanil and sodium hydroxide, and on acidification gave our hemiether. The results of 3 analyses agreed with those for sodium iodoanilate as nearly as could be expected from a substance so unstable that we could purify it only by washing with alcohol, but in spite of this it cannot be sodium iodoanilate, as determinations of the water of crystallization showed that our salt contained 9.95, 9.96%, the iodoanilate 20.12, 20.25%, so that, although the sodium determinations tell against the hemiether hypothesis, the amounts of water furnish us another strong argument in favor of it. To reconcile the two we feel obliged to assign to the salt the somewhat improbable formula, II, $[C_6I_2(ONa)O(OHONa)]_2O$, in which one molecule of sodium hydroxide has been added to one of the quinone oxygens; and we do this in face of a serious objection based

on the color of the salt, which as a hemiacetal ought to be lighter than the free acid, whereas it is darker—purple instead of red.

(5) The hemiether begins to decompose at 215° (uncorr.), iodoanilic acid at 205° (uncorr.); but if our substance were impure iodoanilic acid, it would melt below, not above, the pure substance. The five arguments just given seem to us to prove that our compound is the hemiether of iodoanilic acid.

The hemiether passes with great ease into iodoanilic acid, or its derivatives; water, or sodium hydroxide, gives two molecules of the acid; acetic anhydride diiododiacetoxyquinone; aniline, dianilinoquinone by saponification of the hemiether followed by replacement of the hydroxyls by aniline radicals and the atoms of iodine by hydrogen (two interesting exhibitions of the loosening effect of quinone oxygen).

When the sodium hydroxide acting on the iodoanil was dissolved in 50 parts of alcohol to 10 of water, a different result was obtained from that given by the previous experiments with 15 of alcohol and 30 of water, for, on adding an acid, a product was precipitated, which decomposed between 160° and 180° , and contained the ethoxy group. In our opinion this is diiodohydroxyethoxyquinone (monoethylether of iodoanilic acid), III, $C_6I_2(OH)(OC_2H_5)O_2$, although the formula, IV, $[C_6I_2(OC_2H_5)O_2]_2O$, must also be considered, according to which it is the ethyl ether of the hemiether formed when less alcohol is present. Most of our observations agree equally well, or rather equally badly with either of these formulas, showing, however, a slight preference for III, but there is one which seems to us to pronounce distinctly in favor of III, so we have adopted it, although we cannot claim that it rests on a very secure foundation. This single observation, that we cannot bring into harmony with IV, is the formation of what seems to be diiododiethoxyquinone, $C_6I_2(OC_2H_5)_2O_2$, by the action of ethyl bromide on the silver, or potassium, salt of our substance. The observations telling in favor of III but not excluding IV are the following: Although the percentages of iodine for the two formulas differ by 1.3%, we could not decide between them in this way, as our results covered the whole interval. The specimens most frequently crystallized, however, and, therefore the purest, came nearest to III; and yet, if IV were correct, this could be explained on the supposition that the hemiether was slowly converted into the hydroxyl compound by the water in the solvent— $[C_6I_2(C_2H_5O)O_2]_2O^*$ to $C_6I_2(C_2H_5O)(HO)O_2$ —as observed with the hydroxyhemiether; but such a reaction should be accompanied by a change in properties, and, as none was observed, its occurrence is very doubtful, so that the best explanation of the phenomena is that the change in composition was due to purification and that III is the true formula. This view is supported by the fact that analyses of the silver salt and of the free substance prepared from the hemiacetal gave

results agreeing with III, since both these products should be especially pure.

The most striking derivative of our compound was a bluish black potassium salt, which was stable enough to be crystallized from alcohol, and could be prepared by the action of potassium hydroxide on the free acid or on iodoanil itself. The analyses of this salt gave results nearly 2% too low for the amount of iodine in $C_6I_2(OC_2H_5)(OK)O_2$, and in order to make them agree with III it is necessary to assume one molecule of water in the salt, which seems improbable, since it was dried at 100° . Unfortunately we could not test this assumption by experiment, as the substance began to decompose at higher temperatures. On the other hand the percentages found agree with those calculated for the salt of IV, $[C_6I_2(OC_2H_5)(OHOK)O_2]_2O$. This formula is certainly a strange one, yet it will be remembered that we were driven to adopt a similar one in studying the hydroxyhemioether, although such a salt, being related to the hemiacetals, should be lighter in color than the quinone, and in both cases it was darker, here black from an orange-red quinone. On the other hand, with III we should expect a darker salt from the frequent auxochrome effect of salt formation. Again, if a hemiacetal, the salt should have but a slight stability, whereas it can be crystallized from alcohol without decomposition. Of the two rather doubtful hypotheses, therefore, it seems to us the presence of water required by III is the more probable.

Aniline acting on the free substance converts it easily into the salt $C_6I_2(C_6H_5NH)(OHNH_2C_6H_5)O_2$, which gives with acids the dark blue diiodoanilinoxyquinone, $C_6I_2(C_6H_5NH)(OH)O_2$, whereas potassium hydroxide gives the salt of the unaltered substance. If IV is correct, the feeble aniline must then have split the hemioether to form the aniline salt of the substituted quinone, while the stronger potassium hydroxide has produced no such decomposition. With III no such anomalous assumption is needed, since both aniline and potassium hydroxide simply convert the substances into the corresponding salts.

Acetyl chloride converts the potassium salt into the free acid instead of an acetyl compound, which perhaps agrees better with IV than with III, especially as a similar observation was made with the hydroxyhemioether, but, as this is the only case in which IV is to be preferred, we think that the discussion just given justifies our adoption of III.

The formation of this diiodohydroxyethoxyquinone is not out of harmony with the appearance of the hemioether of iodoanilic acid in the experiments with less alcohol, as each reaction consists in the formation of an ether, the iodine compound reacting with the sodium salt present $-C_6I_2(ONa)_2O_2$ when water is the principal solvent, but with alcohol $NaOC_2H_5$.

It is a curious fact that, whereas the potassium salt $C_6I_2(OC_2H_5)(OK)O_2$ is obtained easily from either the free acid or from iodoanil, the same method with sodium hydroxide converted the free acid into sodium iodoanilate, and with iodoanil produced an unmanageable solution, from which there was little chance of isolating an unstable salt. This striking difference between the behavior of sodium and potassium hydroxides is undoubtedly explained by the slight solubility of the potassium salt, which removed it at once out of the reach of further action, whereas the sodium salt was found to be freely soluble, when at last we succeeded in making it by the action of sodium chloride on the silver salt.

In the action of sodium or potassium hydroxide on iodoanil the product was sometimes the salt, sometimes the iodoanilate, and at others diiododiethoxyquinone, which was the invariable product, when alcohol was the only solvent, while with methyl alcohol the reaction went further, giving the salt of the hemiacetal of diiododimethoxyquinone. It will be interesting to determine whether this greater tendency toward the formation of the methyl than the ethyl hemiacetal appears in other cases.

In general, then, our work has brought out two peculiarities in the behavior of iodoanil with alkaline hydroxides, a tendency toward the replacement of two of its para halogen atoms by different radicals, of which we can find no case with chloroanil or bromoanil, and a tendency toward the replacement of halogen by the ethoxy radical, of which only one case¹ with chloroanil has been recorded, or toward the analogous formation of the hemiacetal. Too much weight should not be put upon these negative results, however, until a more extended study of chloroanil and bromoanil has been made. We have found only one explanation for these differences in effect between iodine and the other halogens, which we give for what it may be worth. According to this the sodium ethylate in the alcoholic sodium hydroxide first forms a diethoxydihalogenquinone, which is afterward saponified more or less completely by the sodium hydroxide. The amount of saponification will depend on the loosening effect of the negative radicals present upon the ethyl groups, and, if the slightly negative iodine is present, after one of the C_2H_5O groups has been converted into NaO , the presence of the sodium in the molecule may well neutralize completely the loosening effect of the iodine, halting the reaction at the diiodohydroxyethoxyquinone, whereas with the much more negative chlorine, or bromine, the sodium would be unable to overcome the loosening effect, so that both ethoxy groups would be saponified.

Our experiments with aniline have thrown some light on the comparative reactivity of different radicals in these substituted quinones. The hydroxy group assists the replacement of an ethoxy group in the para position, $C_6I_2(C_2H_5O)(HO)O_2$ gave $C_6I_2(C_6H_5NH)(HO)O_2$, but an ethoxy group pro-

¹ Kehrman, *J. prakt. Chem.*, 39, 318 (1889).

duces no such effect on a second in the para position, aniline showing no action with $C_6I_2(C_2H_5O)_2O_2$. The acetoxy group is more easily replaced than the hydroxy or ethoxy group, as $C_6I_2(C_2H_5O)(C_2H_3O_2)O_2$ gave in the cold $C_6I_2(C_2H_5O)(C_6H_5NH)O_2$; and, since it gives, when hot, $C_6I_2(C_6H_5NH)_2O_2$, it seems as if the anilino group must loosen the ethoxy group.

The retention of iodine in the ring, when aniline converts the diiodoethoxyacetoxyquinone into diiododianilinoquinone is certainly strange, because the diiodoanilinoacetoxyquinone and the hemiether of iodoanilic acid both give dianilinoquinone (free from iodine), when treated with aniline.

A study of the colors of these compounds shows that in the quinones with oxygen radicals the salts are more deeply colored than the free quinones; $[C_6I_2(OH)O_2]_2O$ and $C_6I_2(C_2H_5O)(OH)O_2$ are red, their salts black. With a nitrogen radical exactly the reverse is the case, the quinone being more deeply colored than the salt; $C_6I_2(C_6H_5NH)(OH)O_2$ is navy blue, the salts red. This seems to be a rule of general application with para-quinones containing halogens, since the three halogen anilic acids are lighter colored than their salts, while the chloro-¹ or bromoanilamic² acid is black, its ammonium salt brown.

In these compounds also the color is deeper, when the two para positions are occupied by different radicals, than when they carry two radicals of the same sort.

Different radicals.	The same radical.
$C_6I_2(C_2H_5O)(OH)O_2$, red	$C_6I_2(C_2H_5O)_2O_2$, orange-red
$C_6I_2(C_2H_5O)(OC_2H_3O)O_2$, red	$C_6I_2(OC_2H_3O)_2O_2$, yellow
$C_6I_2(C_2H_5O)(C_6H_5NH)O_2$, blue	$C_6I_2(C_6H_5NH)_2O_2$, brown
$C_6I_2(OH)(C_6H_5NH)O_2$, black	$C_6I_2(OH)_2O_2$ orange-red

We have been able to find only two well marked cases of this kind in the literature. $C_6Br_2(OH)(NH_2)O_2$ is almost black, while $C_6Br_2(NH_2)_2O_2$ is brownish red and bromoanilic acid reddish. $C_6H_2(OH)(C_6H_5NH)O_2$ is blue, $C_6H_2(C_6H_5NH)_2O_2$ reddish brown and $C_6H_2(OH)_2O_2$ dark yellow.

Experimental.

Action of Sodium Hydroxide on Iodoanil.—The product obtained differs with the amount of alcohol present. We shall begin our account of these reactions with the case, where the quantity of alcohol is small.

The Hemiether of Iodoanilic acid, $[C_6I_2(OH)O_2]_2O$.—Ten grams of iodoanil,³ suspended in a mixture of 15 cc. of alcohol and 30 cc. of water, were treated with 15 cc. of a 50% aqueous solution of sodium hydroxide. A reaction accompanied with evolution of heat took place at once, forming a deep brownish red solution and giving off a disagreeable penetrating

¹ Erdmann, *Ann.*, 48, 321.

² Stenhouse, *Ibid.*, 91, 313.

³ Prepared as described in THIS JOURNAL, 36, 305 (1914).

smell. The addition of dilute sulfuric acid at this point threw down an orange-red precipitate of the hemiether, which was washed with water, until a purple color in the filtrate showed that the substance was beginning to dissolve, after which it was crystallized twice from toluene (Analysis I). A better way of preparing the substance consisted in shaking the solution of the iodoanil in the sodium hydroxide for several minutes, when the sodium salt of the hemiether began to crystallize, and, after the deposition was complete, it was filtered out, washed with alcohol (in which it was practically insoluble) and then dissolved in a small quantity of water, acidified with dilute sulfuric acid, and purified as described above. The substance was dried at 100° ; II, III, IV.

Subst., I, 0.2066; II, 0.2124; III, 0.2338; IV, 0.2312. AgI, 0.2550, 0.2616, 0.2896, 0.2835.

Calculated $[\text{C}_6\text{I}_2(\text{OH})\text{O}_2]_2\text{O}$: I, 66.30. $\text{C}_6\text{I}_2(\text{OH})_2\text{O}_2$, I, 64.78.

Found: I, I, 66.72; II, 66.58; III, 66.96; IV, 66.28.

Attempts to determine the amount of toluene of crystallization gave no results worth recording, because it was held so loosely that it was impossible to dry the crystals with certainty. It seemed to amount to 3 or more molecules.

To determine whether the high percentages of iodine obtained were due to a new compound (the hemiether), or to iodoanilic acid containing an impurity richer in iodine the following tests were made with a specimen of the substance. The only probable impurities of this sort are iodoanil and sodium iodide. To test for sodium iodide the substance was treated with 25 cc. of water in the cold, after which the undissolved portion was filtered out, and what had dissolved precipitated by the addition of nitric acid. Silver nitrate then gave only an insignificant precipitate, which was evidently silver iodoanilate from its red color. As the presence of over 5% of sodium iodide would be necessary to raise the percentage of iodine from 64.78 in iodoanilic acid to the 66.50% found, it is evident that the cause of the high percentage of iodine is not sodium iodide. The residue from this treatment with water was then dissolved in more water, and upon filtration no insoluble residue was obtained, showing the absence of iodoanil. To detect any sodium iodide, which might have escaped the first test by imprisonment in the crystals, the complete solution was boiled until the substance had been converted into iodoanilic acid, which was then precipitated by acidification, and the filtrate treated with silver nitrate, giving, as before, nothing but a very slight red precipitate of silver iodoanilate. Our substance, therefore, was free from an impurity of sodium iodide or iodoanil.

Properties of the Hemiether of Iodoanilic Acid.—It crystallizes from warm toluene in red needles, often spindle-shaped, which we believe to be free from toluene of crystallization; but the crystals deposited, after the solu-

tion has grown cool, differ from these, as they are orange-red, diamond-shaped plates with the obtuse angles truncated, and contain toluene of crystallization, which is given off rapidly on exposure to the air, leaving a salmon colored powder resembling litharge. On longer exposure to the air the substance turns brownish black, but this change does not take place, if it is kept in a desiccator. It begins to decompose at 215° (uncorr.), therefore 10° above the decomposition point of iodoanilic acid. It is soluble in water forming a purple solution like that of iodoanilic acid, and is thrown out of this solution by the addition of sulfuric, or hydrochloric acid; boiling with water converts it into iodoanilic acid. It is much more soluble in alcohol than in water, and the solution shows a strong red color, in this respect also resembling iodoanilic acid; soluble in ether, acetone, ethyl acetate, glacial acetic acid, nitrobenzene, or aniline; nearly insoluble in cold, more soluble in hot chloroform, carbon disulfide, benzene, or toluene; essentially insoluble in naphtha, whether hot or cold. Toluene is the best solvent for it. Cold strong hydrochloric acid or sulfuric acid has no visible effect on it, but when heated an orange solution is formed, which remains unchanged on cooling. Hot, strong nitric acid oxidizes it vigorously with separation of iodine. Dilute sodium hydroxide forms a reddish purple solution.

Action of Hot Water on the Hemiether.—Two grams of the substance were warmed with water until they had dissolved completely, and the solution was then kept just below the boiling point for five minutes. After cooling, sulfuric acid was added, and the salmon colored precipitate crystallized twice from toluene and dried at 100° , when an analysis proved that it was iodoanilic acid, $C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.03. The iodoanilic acid thus prepared resembled the hemiether closely, for, when dissolved in hot toluene, it gave long, thin, red needles (although no spindles) and at a lower temperature red, diamond-shaped plates containing very loosely attached toluene of crystallization (but not truncated on the obtuse angles). These left a salmon-colored powder identical with that from the hemiether, if dried at ordinary temperatures, but the powder was red if heat was used. The rhombic crystals darkened if exposed to the air for some days, but remained unaltered in the desiccator. The iodoanilic acid decomposed at 205° (uncorr.), but this point was not definite enough to be used to distinguish it from the hemiether, so that in all our work we resorted to analysis of the free acid, purified as described above, in order to identify iodoanilic acid.

Sodium Salt of the Hemiether of Iodoanilic acid,

$[C_6I_2(ONa)O(OHONa)]_2O$.—Owing to the very slight stability of the salt its preparation could not be achieved from the hemiether. Thus, 15 grams of the hemiether suspended in 20 cc. of water gave with 4 cc. of 10% sodium hydroxide solution a deep purple liquid, which was sodium iodo-

anilate ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.20). The same result was obtained, if enough sodium hydroxide was used to precipitate the salt at once ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.06). The sodium hydroxide, therefore, has split the hemiether into two molecules of iodoanilic acid; and it was the same with potassium hydroxide in the proportion of 4 molecules to one ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.35). Nor were we more successful when we avoided an excess of alkali by using one gram of the hemiether suspended in a saturated solution of it, and adding potassium hydroxide, so as to have one molecule for each molecule of the hemiether in this gram of it, but the alkali, instead of forming the monopotassium salt, converted the hemiether into potassium iodoanilate, until it was exhausted.

As, therefore, there was no hope of forming its salt from the free hemiether, we turned our attention to the compound obtained directly from iodoanil and sodium hydroxide, which must be the salt of the hemiether, because this substance is obtained from it by acidification. It was prepared as follows: Ten grams of iodoanil, suspended in a mixture of 15 cc. of alcohol and 30 cc. of water, were treated with 15 cc. of a 50% solution of sodium hydroxide. The iodoanil passed slowly into solution with evolution of heat, but upon shaking the liquid vigorously for several minutes the sodium salt began to separate, and seemed to be completely formed after standing for half an hour, when it was filtered out, and washed with alcohol to remove sodium hydroxide and iodide, then warmed with benzene to dissolve any unchanged iodoanil, after which it was air-dried for analysis.

This very unsatisfactory purification was all we could use owing to the instability of the salt. Boiling with water for a few minutes converted it into sodium iodoanilate ($C_6I_2(OH)_2O_2$, I, 64.78). Found, 64.90, while on longer boiling an odor of iodine was observed. Two crystallizations from alcohol and water also gave the iodoanilate ($C_6I_2(OH)_2O_2$, I, 64.78. Found, 65.24) and washing with warm alcohol reduced its iodine by 10%.

Salt of the Hemiether Air Dried.—Subst., 0.4364, 0.4984. Loss at 100°, 0.0434, 0.0496.

Calculated $[C_6I_2(ONa)O(OHONa)]_2O \cdot 5H_2O$: H_2O , 9.13.

Found: H_2O , 9.95, 9.96.

Sodium Iodoanilate Air Dried.—Subst., 0.3926, 0.4750. Loss at 100°, 0.0792, 0.0962.

Calculated $C_6I_2(ONa)_2O_2 \cdot 6H_2O$: H_2O , 19.86.

Found: H_2O , 20.12, 20.25.

The sodium iodoanilate, therefore, contains twice as much water as the salt of the hemiether.

Salt of the Hemiether dried at 100°.

Calculated $[C_6I_2(ONa)O(OHONa)]_2O$: Na, 10.34; I, 57.09.

Found: Na, 9.85, 9.90, I, 55.90.

These results are as good as could be expected from a salt, which could be so little purified. $C_6I_2(ONa)_2O_2$ requires Na 10.55, I 58.24, so that the results would have to be much nearer to decide between these two

formulas, but with our other observations they do establish the peculiar formula given above, as explained in the introduction.

Properties of the Sodium Salt of the Hemiether of Iodoanilic Acid.—It crystallizes in purple prisms terminated at each end by two planes at an obtuse angle. At 100° it loses its water of crystallization, and is converted into a black powder with a tinge of purple. It dissolves freely in water, and the solution might be mistaken for one of potassium permanganate; boiling this solution converts it into sodium iodoanilate; the salt of the hemiether is practically insoluble in alcohol, but decomposed by it when warm. Crystallization from a mixture of alcohol and water converts it into iodoanilate. An excess of sodium hydroxide precipitates it from its solutions.

These properties are essentially the same as those of sodium iodoanilate, except that when anhydrous it is dark brownish purple instead of black.

Action of Aniline on the Hemiether of Iodoanilic Acid.—Two grams of the hemiether dissolved in alcohol were treated with aniline drop by drop, until there was no further precipitation, and the light salmon colored product was washed with alcohol and dried *in vacuo*.

Calc. $C_6I_2(OH\text{NH}_2C_6H_5)_2O_2$: I, 43.82. Found: 43.34.

According to this analysis it is aniline iodoanilate, but its properties throw some doubt on this conclusion. The light salmon color is strange for an iodoanilate, and so are the facts that dilute sulfuric acid has no action on it, and sodium hydroxide very little in the cold; both, however, give iodoanilic acid if hot. More experimental work, therefore, is needed, before its nature can be considered settled.

If the hemiether was warmed with aniline it dissolved more quickly than in the cold, and the dark brown liquid deposited scales, which, after the addition of a little alcohol, were filtered, and washed with alcohol, when they were recognized as dianilinoquinone by the absence of halogen, the characteristic purple scales, and the carmine-red color with strong sulfuric acid, identical with the properties shown by a specimen of dianilinoquinone prepared in the usual way.

Diiododiacetoxyquinone, $C_6I_2(C_2H_3O_2)_2O_2$.—This substance was formed when 2 grams of the hemiether were mixed with acetic anhydride in the proportion of 1 molecule to 5, and the mixture warmed, until all the hemiether had gone into solution. A yellow solid was deposited as the liquid cooled, which was freed from most of the acetic anhydride by standing on a porous plate *in vacuo* over potassium hydroxide. It was then crystallized several times from a mixture of 3 parts naphtha and one part of benzene, and dried *in vacuo*.

Calculated $C_6I_2(C_2H_3O_2)_2O_2$: I, 53.34. Found: 53.87.

Properties of Diiododiacetoxyquinone.—It crystallizes from benzene and

naphtha in brilliant square yellow plates, which begin to decompose at 190° giving off violet vapors, and melt at 270° (uncorr.). It is easily soluble in alcohol, ethylacetate, glacial acetic acid, carbon tetrachloride, benzene, or toluene, essentially insoluble in naphtha. Cold water saponifies it slowly, warm water quickly into iodoanilic acid; cold dilute sodium hydroxide saponifies it immediately.

That this substance was a derivative of iodoanilic acid and not of the hemiether was shown by the fact that it was identical in every respect with a specimen prepared earlier from acetic anhydride and iodoanilic acid.

Calculated $C_6I_2(C_2H_5O_2)_2O_2$: I, 53.34. Found: 53.51.

When the sodium salt of the hemiether was treated with acetyl chloride we obtained the free hemiether.

Calculated $[C_6I_2OHO_2]_2$: I, 66.32. Found: 66.58.

This experiment seems to show that acetyl chloride does not act easily on the hemiether.

Action of Hot Sodium Hydroxide on Iodoanil.—If the mixture of sodium hydroxide and iodoanil was boiled for a minute, the product was sodium iodoanilate.

Calculated $C_6I_2(OH)_2O_2$: I, 64.78. Found: 65.25.

Diiodohydroxyethoxyparaquinone, $C_6I_2(OH)(OC_2H_5)_2O_2$.—Ten grams of iodoanil were suspended in 50 cc. of alcohol, and treated in the cold with 10 cc. of a 50% solution of sodium hydroxide all in one portion. Upon shaking, the iodoanil went into solution rapidly with evolution of heat, and the greenish black liquid gave off a disagreeable penetrating smell like that observed in the preparation of the hemiether; three to four times its volume of water was then added, when upon acidification with dilute sulfuric acid a reddish orange precipitate was thrown down, which was washed with water till the filtrate began to turn purple, and then crystallized three times from naphtha. The diiodohydroxyethoxyquinone was dried at 80° for analysis.

In preparing this compound it is necessary to add the whole of the sodium hydroxide at once. If, instead, it is added in small portions at a time with shaking after each addition, the orange-red precipitate obtained on acidification did not crystallize from naphtha in the clusters of red needles, which show that the reaction has gone normally, but in small crystals, or sometimes it separated in an amorphous state. Such a product was separated by cold alcohol into two portions, the more soluble of which was the monoethylether, while the residue after crystallization from hot alcohol melted at 185° showing that it was the diiododiethoxyquinone.

Analyses of diiodohydroxyethoxyquinone.

Subst., 0.2300, 0.1836, 0.2110, 0.2076, 0.2508. AgI, 0.2658, 0.2092, 0.2382, 0.2348, 0.2822. Calc. $[\text{C}_6\text{I}_2\text{OC}_2\text{H}_5\text{O}_2]_2\text{O}$: I, 61.78; $\text{C}_6\text{I}_2\text{OHOC}_2\text{H}_5\text{O}_2$: I, 60.42. Found: I, 62.47; II, 61.59; III, 61.02; IV, 61.14; V, 60.82.

The specimens used in I and II were crystallized 3 times, those in III and IV 6, that in V 8 times.

Properties of Diiodohydroxyethoxyquinone.—It crystallizes from naphtha in rosettes of brilliant long red needles, which after several days exposure to the air lose their luster and turn reddish black, but remain unchanged in the desiccator. It begins to decompose at 160° , but does not melt completely till 180° (uncorr.). It is soluble in alcohol, ether, chloroform, tetrachloride of carbon, glacial acetic acid, carbon disulfide, benzene, toluene, ethylacetate or nitrobenzene, almost insoluble in cold, soluble in hot naphtha; water in the cold dissolves it slowly forming a purple solution, in boiling water it dissolves easily, but if the solution is boiled a short time decomposition takes place attended with separation of iodine and the formation of a dark brown solution. Strong hydrochloric acid produces no visible effect on it; strong sulfuric acid dissolves it with a dark brown color; strong nitric acid, if gently warmed, decomposes it with separation of iodine. The action of alkalis is described in detail in the following sections.

Potassium Salt of Diiodohydroxyethoxyquinone, $\text{C}_6\text{I}_2(\text{OK})(\text{OC}_2\text{H}_5)_2\text{O}_2\text{H}_2\text{O}$.—Two grams of the monoethyl compound were treated in the cold with an excess of a 10% solution of potassium hydroxide, when, after standing for several minutes, a black mass was precipitated, which, although nearly insoluble in the excess of alkali, imparted a pink color to the liquid. The solid was freed from potassium hydroxide by washing with a small quantity of water, until it began to dissolve, after which the washing was continued with a few drops of alcohol, and the purification concluded by crystallization from alcohol twice for I and III, four times for II.

Subst., 0.2298, 0.1566, 0.6758, AgI, 0.2284, 0.1552; K_2SO_4 , 0.1206. Calc. for $\text{C}_6\text{I}_2\text{OKOC}_2\text{H}_5\text{O}_2$: I, 55.42; K, 8.54; for $\text{C}_6\text{I}_2\text{OKOC}_2\text{H}_5\text{O}_2\text{H}_2\text{O}$: I, 53.33; K, 8.21; for $[\text{C}_6\text{I}_2(\text{OK})(\text{OC}_2\text{H}_5)\text{O}(\text{OKOH})]_2\text{O}$: I, 54.38; K, 8.37. Found: I, I, 53.72; II, 53.57; K, III, 8.01.

It was impossible to determine experimentally, whether water of crystallization was retained at 100° , as it decomposed slowly, when heated to higher temperatures.

The same compound was also obtained as follows: Ten grams of iodoanil, suspended in 80 cc. of alcohol, were treated with 20 cc. of a solution of 15 grams of potassium hydroxide in 100 cc. of alcohol. The iodoanil dissolved immediately, and after being heated just below boiling for several minutes the solution changed from dark reddish purple to blackish purple. It was then allowed to stand at rest, and, if the experiment had succeeded, the solution was converted in a few minutes into a mass of

black crystals, which were washed with a little alcohol, and then after warming with successive portions of benzene, until no more color was removed, were recrystallized three times from alcohol, and dried at 100° .

Subst., 0.2028, 0.1896, 0.2356, 0.3752; AgI, 0.2022, 0.1888, 0.2328; K_2SO_4 , 0.0632.
Calc. for $C_8I_2OC_2H_5OKO_2H_2O$: I, 53.33; K, 8.21. Found: I, 53.88, 53.82, 53.39; K, 7.56.

This formation of the potassium salt direct from iodoanil cannot be recommended as a method for its preparation, since the conditions, under which it takes place, are so delicately balanced that the process frequently miscarries. If the first solution of the iodoanil was greenish instead of reddish black, the product was more or less contaminated with either potassium iodoanilate ($C_8I_2(OH)_2O_2$, I, 64.78; found, 63.98) or diiodo-diethoxyquinone, which was precipitated as an orange-red compound, sometimes the only product of the reaction, identified by its melting point 186° after several crystallizations from alcohol.

Properties of the Potassium Salt of Diiodohydroxyethoxyquinone.—It crystallizes from alcohol in bluish black needles, which are black after drying. It dissolves freely in water forming a dark solution much like that of potassium permanganate, which is not alkaline to test paper, and does not become so even after boiling for several minutes. Potassium hydroxide precipitates it from this solution, even when present in comparatively small amount, but on warming the mixture potassium iodoanilate is formed. It is slightly soluble in cold alcohol, freely in hot; insoluble in ether, chloroform, naphtha, benzene, or toluene; essentially insoluble in cold nitrobenzene, or aniline, but dissolves on warming; soluble in acetone, ethylacetate, or glacial acetic acid. Alcohol is the best solvent for it, as crystallization from this substance is not attended by perceptible decomposition. Dilute acids set free the diiodohydroxyethoxyquinone. Strong nitric acid acts on it with sufficient violence to set it on fire. With alcoholic sodium ethylate the black salt forms a yellow solution, from which acid throws down a white precipitate evidently a hemiacetal, since it turns orange-red on gentle warming with dilute sulfuric acid.

Attempts to Make the Sodium Salt.—None of our attempts to make the sodium salt by the methods, which had furnished the potassium salt easily, led to the desired result. Thus when the free substance was treated in the cold with a few drops of a 10% solution of sodium hydroxide, sodium iodoanilate was formed ($C_8I_2(OH)_2O_2$, I, 64.78; found, 65.14). The same result was obtained, when the substance was heated with successive small portions of dilute sodium hydroxide (found, 64.99).

Ten grams of iodoanil suspended in 50 cc. of alcohol and gently warmed with 15 cc. of a saturated alcoholic solution of sodium hydroxide gave a greenish black solution, from which water threw down a precipitate of

diiododiethoxyquinone, identified by its melting point, 186°. If methyl alcohol was used as the solvent, much heat was given out by the reaction, and water added to the hot solution precipitated diiododimethoxyquinone recognized by its orange-red color and melting point 195°; but if the solution was cooled, and then acidified, a white precipitate was obtained, shown to be the diiododimethoxyquinonedimethylhemiacetal of Torrey and Hunter¹ by its solubility in sodium hydroxide solution, and the great ease with which heat, or a dilute acid converted it into the diiododimethoxyquinone melting at 195°.

We finally succeeded in preparing a pure solution of the sodium salt by treating the silver salt with sodium chloride, but we did not obtain it in the solid state.

Silver Salt of Diiodohydroxyethoxyquinone $C_6I_2(OAg)(OC_2H_5)_2O_2$.—A specimen of the potassium salt which had been crystallized once from alcohol, was dissolved in water, and treated with a solution of silver nitrate until there was no further precipitation. The brown solid thus obtained was washed by decantation, until it was free from silver nitrate, and dried on a porous plate in a desiccator.

Subst., 0.2126; AgI, 0.1894. $[C_6I_2OC_2H_5OAgOHO]_2O$: I, 47.38; $C_6I_2OC_2H_5OAgO_2$, I, 48.19. Found: 48.16.

A specimen dried at 100° turned somewhat purple, which was evidently due to decomposition, as it contained 1% more iodine than the salt analyzed above.

Properties of the Silver Salt of Diiodohydroxyethoxyquinone.—It is a brown solid, which is somewhat decomposed, if dried at 100°. It is very slightly soluble in water forming a light purple solution; insoluble in cold alcohol, barely soluble in hot. Cold dilute nitric acid does not act on it, but when hot decomposes it with formation of silver iodide. Potassium hydroxide does not act in the cold, but on warming gives a brownish red solution and silver oxide. Ammonium hydroxide dissolves it easily forming a red solution. Potassium chloride gives silver chloride and the potassium salt recognized by its bluish black color and solubility in alcohol; sodium chloride in saturated solution acts in the same way. The solution of the sodium salt was dark purple. It was more soluble in alcohol than the potassium salt.

When the silver salt was heated with ethyl bromide in a sealed tube at 100° for 6 to 8 hours, silver bromide was formed, and the other product, which was orange-red, was freed from the excess of ethyl bromide by spontaneous evaporation, and then crystallized 7 times from alcohol, when it showed the melting point 183°. The amount left was too small for further crystallization, or analysis, but we think it safe to infer that it was diiododiethoxyquinone which melts at 186°. Frequently iodoanilic

¹ THIS JOURNAL, 34, 702 (1912).

acid appeared also in these experiments. When the potassium salt was heated to 100° for 36 hours with ethyl bromide, a little diiododiethoxyquinone was formed, but the yield was exceedingly small.

An aqueous solution of the potassium salt ($C_6I_2OC_2H_5OKO_2$) gave, after standing an hour with barium nitrate, a small bluish black precipitate of the barium salt, which proved to be moderately soluble in water, or alcohol. With calcium nitrate no precipitate was formed, but on the addition of alcohol a small amount of a bluish black calcium salt was obtained. The copper salt was light green.

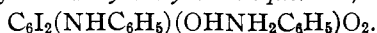
Diiodohydroxyethoxyquinonethylhemiacetal.—When an alcoholic solution of sodium ethylate was added to diiodohydroxyethoxyquinone in very small quantities at a time, a blackish purple mass was formed at first, but upon adding more of the sodium ethylate the whole went into solution with an orange-brown color, and then the addition of a dilute acid threw down a white precipitate, which could be dissolved in sodium hydroxide, and reprecipitated with dilute acid. No attempt was made to analyze it, as its instability forbade thorough purification, even the best specimens we obtained showing an orange tint. That it was the expected hemiacetal, however, was shown by its properties, and especially by its decomposition with dilute acid, which on gentle warming converted it into an orange-red compound, and this after 5 crystallizations from naphtha was proved to be the diiodohydroxyethoxyquinone.

Subst., 0.2090, 0.2760; AgI, 0.2354, 0.3108. Calc. $C_6I_2OC_2H_5OHO_2$: I, 60.45. Found: I, 60.88, 60.87.

It would seem from these results that the conversion into the hemiacetal was an excellent method of purifying the diiodohydroxyethoxyquinone.

Properties of Diiodohydroxyethoxyethylhemiacetal.—It is probably white when pure, but we did not succeed in obtaining it dry without an orange tint. It is soluble in alcohol, ether, chloroform, ethyl acetate, or benzene; essentially insoluble in naphtha, carbon disulfide, toluene, or water; on warming with water an orange-red solid is obtained, and the liquid is colored dark purple by iodoanilic acid. When heated to 100° , it is converted into the diiodohydroxyethoxyquinone, and the same change is brought about by gentle warming with dilute acids. In fact, the substance shows a strong tendency to lose alcohol under most conditions. Acetic anhydride forms with it a red solution. It dissolves easily in sodium hydroxide forming the sodium salt, but this was so soluble that we made no attempt to isolate it.

The Aniline Salt of Diiodohydroxyanilinoquinone,



—When 2 grams of diiodohydroxyethoxyquinone, dissolved in 25 cc. of alcohol, were treated with aniline, the first few drops produced a vivid

dark purple color, and, if the addition of the aniline was continued, until the color ceased to become deeper, after a short time rosettes of brownish purple needles were deposited slowly in the cold, at once when hot, and the dark color disappeared from the solution. The salt was purified by washing with alcohol.

Calculated $C_6I_2NHC_6H_5OHNH_2C_6H_5O_2$: I, 45.33. Found: I, 45.22, 45.52.

Properties of the Aniline Salt.—In its preparation it is obtained from alcohol in rosettes of brownish purple needles, which begin to decompose at 165° , but do not melt even at 285° . It is soluble in ether, acetone, chloroform, ethylacetate, or glacial acetic acid; essentially insoluble in cold alcohol, tetrachloride of carbon, naphtha, benzene, toluene, or nitrobenzene, but dissolves in any of these solvents when hot; insoluble in water. The solutions are purple, but we found it impossible to crystallize the salt without decomposition from any of its solvents. Dilute acids set free the diiodohydroxyanilinoquinone. Hot strong nitric acid oxidizes it setting free iodine. The action of acetic anhydride will be described later.

Diiodohydroxyanilinoquinone, $C_6I_2(OH)(C_6H_5NH)O_2$.—Two grams of the aniline salt were treated with 30 cc. of dilute sulfuric acid, when the color changed at once to a deep blue turning black in a few minutes. The filtrate was proved to contain aniline by treatment with bromine. The solid after washing with water and finally with a little alcohol was recrystallized several times from toluene and, dried at 100° .

Subst., 0.2068, 0.2345; AgI, 0.2066, 0.2362. Calc. $C_6I_2OHC_6H_5NHO_2$: I, 54.37.

Found: 54.00, 54.45.

Properties of Diiodohydroxyanilinoquinone.—It forms very small navy blue crystals, which decompose at about 190° . It is slightly soluble in alcohol, chloroform, glacial acetic acid, benzene, toluene, or nitrobenzene; easily soluble in ether, ethyl acetate, or acetone; essentially insoluble in naphtha, or in cold carbon disulfide, soluble in the latter when hot. Hot nitric acid forms an orange-red solution with it. Sodium hydroxide dissolves it forming a dark red solution of the salt, from which an acid throws down the original substance. This sodium salt could be obtained as a dark red solid by treating the free compound with ether and sodium ethylate; it is freely soluble in water, or alcohol, and is converted by exposure to the air into a blackish red tar. The pyridine salt is brown. The free hydroxy compound, when suspended in alcohol and treated with bromine water, forms an orange solution, which gives a yellow precipitate on dilution.

When the aniline salt $C_6I_2(C_6H_5NH)(OHNH_2C_6H_5)O_2$ was warmed with acetic anhydride a dark blue solution was formed solidifying on cooling to a mass of dark blue crystals, which after crystallization from benzene and naphtha began to decompose at about 170° , and were soluble in most of the organic solvents except naphtha. We believe the substance to be

diiodoacetoxyanilinoquinone from the following observations. With warm sodium hydroxide it formed a dark red solution, and, if heated with aniline, gave dianilinoquinone (recognized by the absence of iodine), its brown color, scale-like crystals from nitrobenzene, and the crimson solution with strong sulfuric acid, being identical in all these respects with a specimen prepared in the usual way.

Diiodoacetoxyethoxyquinone, $C_6I_2(OC_2H_5O)(C_2H_5O)O_2$.—Two grams of the diiodohydroxyethoxyquinone were heated with acetic anhydride in the proportion of one molecule to five, until the whole had gone into solution, when on cooling orange-red crystals were deposited, which, after being freed from acetic anhydride *in vacuo*, were purified by 5 crystallizations from naphtha, and dried at 100° .

Subst., 0.2400, 0.2030; AgI, 0.2454, 0.2082. Calc. $C_6I_2OC_2H_5OOC_2H_5O_2$: I, 54.95.
Found: I, 55.27, 55.44.

Properties of Diiodoacetoxyethoxyquinone.—Brilliant orange-red prisms which melt at 166° (uncorr.) without decomposition. It is soluble in alcohol, ether, chloroform, acetone, ethylacetate, glacial acetic acid, carbon disulfide, benzene, toluene, or nitrobenzene; nearly insoluble in cold naphtha; insoluble in water. Sodium hydroxide converts it into sodium iodoanilate slowly when cold, rapidly when hot. The best solvent for it is hot naphtha.

Although the free substance reacted so easily with acetic anhydride, strangely enough the dry potassium salt was not affected by it in the cold, and gave a black varnish with it on long heating. Acetylchloride in excess converted the salt into diiodohydroxyethoxyquinone (calculated I, 60.45; found, 61.28). As the conversion was complete, it could hardly have been caused by an impurity of hydrochloric acid. It is strange, however, that the excess of acetylchloride did not act on the free hydroxy compound under conditions which gave complete reaction with the anhydride; and also no result was obtained, even when a drop of strong sulfuric acid or a little sodium acetate was used as a catalyzer.

Action of Aniline on Diiodoacetoxyethoxyquinone.—Three grams of the diiodoacetoxyethoxyquinone were dissolved in warm alcohol, and, after the solution had cooled, 2 cc. of aniline were added, when the liquid turned dark red immediately, and deposited a greenish black solid, which was washed with alcohol, as it is only slightly soluble in the cold. Upon treatment with hot alcohol the product was separated into a more soluble black compound, and one which was yellowish brown and nearly insoluble. The black substance, which is the principal product in the cold, was purified by crystallization from alcohol, and dried at 90° .

Subst., 0.2250, 0.1988; AgI, 0.2433, 0.1890. Calc. $C_6I_2NHC_6H_5OC_2H_5O_2$: I, 51.31.
Found: I, 51.57, 51.39.

Properties of Diiodoethoxyanilinoquinone.—It crystallizes from alcohol in long black shining needles, which melt at 182° (uncorr.) with decomposition.

It is soluble in ether, chloroform, acetone, acetic ester, carbon disulfide, benzene, toluene, or nitrobenzene, forming dark purple solutions; slightly soluble in cold, soluble in hot alcohol, which is the best solvent for it. Strong sulfuric acid gives a greenish black solution, turning brownish on standing, sodium hydroxide does not act in the cold, but on warming forms a red solution from which an acid throws down a black substance probably diiodohydroxyanilinoquinone.

The yellowish brown product separated from the preceding by its slight solubility in hot alcohol was formed in small quantity in the cold, but became the principal product, if the aniline was added to a hot alcoholic solution of diiodoacetoxyethoxyquinone. It was purified by crystallization from toluene.

Subst., o.1868; AgI, o.1623. Calc. $C_6I_2(NHC_6H_5)_2O_2$: I, 46.86. Found: I, 46.94.

Properties of Diiododianilinoquinone.—It crystallizes from toluene in dark brown needles decomposing at about 220° . It is slightly soluble in chloroform, acetone, acetic ester, benzene, toluene, nitrobenzene, or aniline, more soluble hot; essentially insoluble in alcohol, ether, carbon disulfide, glacial acetic acid, or naphtha. It is decomposed on warming with sodium hydroxide forming a yellow solution, which with bromine water gives a precipitate of tribromoaniline. The best solvent for it is hot toluene.

Action of Sodium Hydroxide on Bromoanil in Ethyl Alcohol.—Ten grams of bromoanil suspended in 50 cc. of ethyl alcohol were treated with 10 cc. of 50% aqueous sodium hydroxide solution; the solid dissolved at once, and soon deposited purple needles of sodium bromoanilate, recognized by the analysis of the free acid after it had been crystallized several times from toluene ($C_6Br_2(OH)_2O_2$, Br 53.69, found Br 53.65). The experiment was repeated several times under varying conditions, but in every case the product was sodium bromoanilate.

In the hope of getting α or β addition compounds similar to those obtained from tetrabromoorthoquinone iodoanil, or bromoanil was allowed to stand for 5 months with methyl alcohol, but no action was observed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 231.]

RESEARCHES ON QUINAZOLINES. XXXII. ON SOME QUINAZOLONES, BENZIMIDAZOLES, AND RELATED COMPOUNDS, DERIVED FROM 5-PSEUDOCUMIDINE.

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I. Introduction, and Discussion of Results.

In continuation of the investigations which have been going on for several years in this laboratory on heterocyclic systems obtainable from