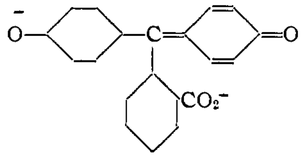
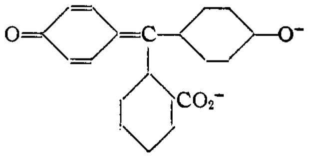
shown to assume color only when the dibasic ion is formed, has then the structure



which can become



by the type of transformation just mentioned. Continuous alternation between the two forms is equivalent to the oscillation of a single electron between the positions. The frequency of such an oscillation might be expected to be less than that of an electron limited in its motion to the dimensions of a single atom, and therefore to give an absorption band in the visible rather than in the ultraviolet. In the case of crystal-violet a similar relation exists between the ions $\overset{+}{\mathbf{R}}$, $+\mathbf{R}$ and $\underset{+}{\mathbf{R}}$, and between $\overset{+}{\underset{H^+}{\mathbf{R}}}$ and $\underset{H^+}{+\mathbf{R}}$, and both these forms, as has been experimentally shown, have great absorbing power. The much weaker color of the yellow ion can be accounted for by its quinoid structure, which is capable of producing a yellow color even where no electronic shift beyond a single benzene ring seems possible.

Rosaniline and para-rosaniline give ions which are similar to those of crystal-violet and may be represented by the same symbols. It is therefore to be expected that the rosanilines would have the same number of absorption bands as crystal-violet and the relative position of the three is indeed found to be the same. The first two absorption bands are, however, much closer together, so that on casual observation the first two colors are hardly distinguishable. In the case of malachite green (which has two amine nitrogens) only the ions $\overset{+}{\mathbf{R}}$ and $+\mathbf{R}$ are related as indicated above; it therefore should have only the two last colors of crystal-violet, and such is again the case. The interesting and important problem remains to apply similar considerations to other derivatives of triphenyl methane and related substances.

BERKELEY, CAL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

CERTAIN DERIVATIVES OF IODOANIL.[1]

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

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This paper contains a description of the conclusion of our work upon

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

the derivatives of iodoanil, which was taken up by one of us (B.) at the suggestion of Professor H. A. Torrey in continuation of his work with Hunter.[1] After the preparation of the diiododimethoxyquinone, diiododiethoxyquinone and silver iodoanilate, Professor Torrey's lamented death made a new arrangement necessary, and accordingly the rest of the work has been carried on by us together.

We have already described[2] the most striking cases in which iodoanil behaves differently from chloro- or bromoanil. The substances described in this paper show a surprising resemblance to the corresponding chlorine or bromine compounds; the color, for instance, is essentially the same, although, in other cases, iodine has shown a marked tendency to deepen color, and no qualitative difference was observed in the solubilities. Torrey and Hunter[1] found, with the dihalogendiphenoxyquinones, that the melting point of the bromine compound lay half way between those of the chlorine and iodine compounds, and that the same was true of the cresoxy derivatives. In the hope of finding similar regularities, we have prepared several series of dihalogenquinones, the melting points of which are given below:

	$C_6X_2(CH_3O)_2O_2$.	$C_6X_2(C_2H_5O)_2O_2$.	$C_6X_2(C_7H_7O)_2O_2$.
Cl	141–2°[3]	104–5°[3]	142°[6]
Br	175°[4]	139°[5]	146°
I	196°	186°	160°

	$C_6X_2(C_2H_3O_2)_2O_2$.	$C_6X_2(CH(COOC_2H_5)_2)_2O_2$.
Cl	182.5°[7]	132°[8]
Br	205°	109°
I	207°	138°

The only approach to regularity in these melting points is found in the alkyloxy compounds, and here the differences from the expected melting points (+7° and —5°) are too great for us to admit the existence of such a regularity. In the dimalonic ester quinones, the melting point of the bromine compound is even lower than that of the chlorine derivative. These data, therefore, indicate that the relation of the melting points observed by Torrey and Hunter is a special case and not part of a general law applying to all quinones containing halogens.

The derivatives mentioned above, with the exception of the diaceto compounds, were made by the action of the reagent on the diiododiphen-

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[1] This Journal, 34, 702 (1912).

[2] "Octoiodoquinhydrone," This Journal, 36, 301 (1914); "Action of Alkaline Hydroxides on Iodoanil," This Journal, 36, 551 (1914).

[3] Kehrmann, *J. prakt. Chem.*, 40, 365 (1889).

[4] Will, *Ber.*, 21, 608 (1888).

[5] Bentley, *Am. Chem. J.*, 20, 479 (1898).

[6] Jackson, Oenslager, *Ibid.*, 18, 12 (1896).

[7] Nef, *J. prakt. Chem.*, 42, 170 (1890).

[8] Stieglitz, *Am. Chem. J.*, 13, 38 (1891).

oxyquinone, since we found, as with the chlorine derivatives,[1] that in this case the reaction ran smoothly with an almost quantitative yield, whereas, if the reagent acted directly on the iodoanil, the yields were small and the product hard to purify. The diiododianilinoquinone, melting with decomposition at 240° (uncor.), and the diiododi-*p*-toluidinoquinone decomposing at 205° (uncor.) were also prepared in this way. In making the dimethoxy- and diethoxy-compounds the first products were the corresponding diiododialkyloxyquinone hemiacetals, which dropped into the quinones, when heated for a short time with acetic anhydride. This is worth noting, since the dichlorodimethoxy-*p*-quinone dimethylhemiacetal is decomposed in the same way,[1] indicating that the hemiacetals of the para series are less stable than those derived from the *o*-quinones, which, to judge from four examples, are not decomposed by acetic anhydride; but give acetyl derivatives, if monohemiacetals,[2] or show no action in the case of the one dihemiacetal[3] we can find.

In making the benzyloxy compound, alcohol must be carefully excluded. On one occasion, when dried but unwashed ether was used as the diluent, the product was exclusively the ethyl compound; and that it is equally susceptible to the action of water is shown by the formation of sodium iodoanilate as a secondary product, when the substance was prepared with sodium, benzyl alcohol, and dry benzene, as we can find no source for this except the atmospheric moisture absorbed through the return condenser during the 2 hours' boiling.

The silver salt of iodoanilic acid is interesting, because it is insoluble in dilute nitric acid, or even in cold, strong nitric acid, which, however, if hot, decomposes it, forming silver iodide.

As with other quinones, phenylhydrazine acted as an excellent reducing agent. In this way we prepared diiododiphenoxyhydroquinone melting with decomposition at 260° (uncor.), tetraiodohydroquinone melting with decomposition at 258° (uncor.), and dibromohydroquinonedimalonic ester melting at 183° (uncor.). From the tetraiodohydroquinone the diacetate was made with acetic anhydride, which begins to decompose at 270°, and melts at 285° (uncor.), a behavior we did not expect from a diaceto compound. The same product was obtained from iodoanil and acetic anhydride, if the action was helped by a few drops of strong sulfuric acid. Such a reaction seems to be a general one for the *p*-quinones, as acetohydroquinones have been obtained by Sarauw[4] with quinone and acetic anhydride at 260°, or according to Buschka[5] by boiling the two

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[1] Jackson, Grindley, *Am. Chem. J.*, **17**, 579 (1895).

[2] Jackson, MacLaurin, *Am. Chem. J.*, 38, 144 (1907); Jackson, Flint, *Ibid.*, **39**, 85; Jackson, P. S. Carleton, *Ibid.*, **39**, 493 (1908).

[3] Jackson, MacLaurin, *Ibid.*, 38, 157 (1907).

[4] *Ann.*, **209**, 129 (1881).

[5] *Ber.*, **14**, 1327 (1881).

substances with sodium acetate, and by Graebe,[1] when acetyl chloride acted on chloroanil.

When the diiododianilinoquinone was heated with nitrobenzene, the flask was soon filled with vapors of iodine, and the only product we succeeded in isolating from the liquid was a small quantity of dianilinoquinone. We can give no explanation of this curious reaction. If aniline was used instead of nitrobenzene, a considerable yield of dianilinoquinone was obtained, as was to be expected. This reaction had been already observed by Torrey and Hunter,[2] when they caused an excess of aniline to act on diiododiphenoxyquinone.

The diiododiaminoquinone decomposing at 230° (uncor.) was made by the action of alcoholic ammonia on iodoanil. The effect of the quinone oxygen and the iodine on the amino groups is so pronounced that it forms salts with sodium hydroxide but not with dilute acids.

The three dihalogenoquinonedimalonic esters resemble each other closely, all are yellow, and form intensely blue sodium salts soluble in water. Our attempts to saponify them failed, because they are so easily carbonized. Much time was devoted to the study of the decomposition of the sodium salt by cold water, but the amorphous product was so unmanageable that no results worth publishing were obtained. When the dibromoquinonedimalonic ester was treated with bromine and alcohol, a new substance, melting at 172° (uncor.), was formed which can hardly have any formula except $C_6Br_2(CBr(COOC_2H_5)_2)_2O_2$, and is therefore dibromoquinonedibromomalonic ester. This view of its constitution was confirmed by the ease with which the second atoms of bromine were replaced by hydrogen, the change being brought about by longer boiling with alcohol and bromine, a reaction we think perhaps analogous to the reduction of iodo compounds by hydriodic acid, and also by aniline, which at the same time seemed to replace the ring bromine atoms by anilino groups. Sodium hydroxide, or similar reagents, gave a reddish brown solution, from which no definite compound was obtained.

An experiment on the action of chloride of iodine on quinone, instead of the expected iodo compound, gave dichloroquinone, a curious result in view of the fact that the chloride of iodine introduces iodine into a great variety of substances, such as, for instance, resorcinol,[3] catechol,[4] phenol,[5] and aniline.[6]

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[1] *Ann.*, **146**, 12 (1868).

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

[3] Michael, Norton, *Ber.*, **9**, 1752 (1876).

[4] Jackson and Boswell, *Am. Chem. J.*, **35**, 520 (1905).

[5] Schutzenberger, *Jahresb.*, **1865**, 524; Lepetit, *Gazz. chim. ital.*, **20**, 105 (1890).

[6] Stenhouse, *Ann.*, **134**, 213 (1865); Michael and Norton, *Ber.*, **11**, 111 (1878).

Experimental.

The iodoanil was prepared by the method already described.[1] To convert it into diiododiphenoxyquinone 20 g. were treated with the sodium phenolate made by adding 6.2 g. of phenol to 2.6 g. of sodium hydroxide dissolved in 50 cc. of water. After warming for half an hour the product was crystallized once from toluene, which purified it sufficiently for our purposes.

Diiododiphenoxyhydroquinone, $C_6I_2(OC_6H_5)_2(OH)_2$.—Phenylhydrazine was added drop by drop to 2 g. of diiododiphenoxyquinone suspended in hot glacial acetic acid, until no more nitrogen was evolved. The white product was crystallized from benzene or toluene, until it showed the constant melting point 260° (uncor.).

Subs. 0.2370; AgI, 0.2016.
Calc. for $C_6I_2(OC_6H_5)_2(OH)_2$: I, 46.51; found: I, 45.98.

Properties.—Small, white needles from benzene sintering at 255°, melting fully at 260° (uncor.). It is slightly soluble in cold chloroform, acetone, ether, ethyl acetate, glacial acetic acid, nitrobenzene, or aniline; essentially insoluble in cold carbon tetrachloride, benzene, toluene, or naphtha; freely soluble in any of these solvents if heated. Benzene or toluene is the best solvent for it. Sodium hydroxide gives a colorless solution with it, from which an acid throws down the unaltered substance.

Diiododimethoxyquinone, $C_6I_2(OCH_3)_2O_2$.—Torrey and Hunter's[2] diiododimethoxyquinone dimethylhemiacetal (prepared from diiododiphenoxyquinone and sodium methylate) was warmed a few minutes with a little acetic anhydride. On cooling, bright red needles were deposited, which, after drying on a porous plate, were crystallized from methyl alcohol until they showed the constant melting point 196° (uncor.).

Subs. 0.2524, 0.1670; AgI, 0.2834, 0.1874.
Calc. for $C_6I_2(OCH_3)_2O_2$: I, 60.47; found: I, 60.68, 60.64.

Properties.—It crystallizes in light red needles melting at 196° (uncor.). It is easily soluble in acetone, ethyl acetate, carbon tetrachloride, benzene, or toluene; essentially insoluble in ether, cold alcohol, or water. Methyl alcohol is the best solvent for it. Cold water does not attack it, but when hot slowly converts it into iodoanilic acid.

Diiodododiethoxyquinone, $C_6I_2(OC_2H_5)_2O_2$.—This compound was prepared in the same way as the dimethoxy compound. It was crystallized from alcohol till it melted constant at 186° (uncor.).

Subs. 0.2476, 0.1912; AgI, 0.2602, 0.1998.
Calc. for $C_6I_2(OC_2H_5)O_2$; I, 56.69; found, I, 56.79, 56.50.

Properties.—It crystallizes in orange red needles melting at 186° (uncor.). Its solubilities are essentially the same as those of the dimethyl

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[1] THIS JOURNAL, 36, 305 (1914).

[2] *Ibid.*, 34, 702 (1912).

compound. Hot water converts it slowly, sodium hydroxide immediately, into iodoanilic acid.

The diiododiethoxyquinone was also formed in an attempt to make the benzyl derivative by the action of diiododiphenoxyquinone with sodium benzylate made by treating benzyl alcohol dissolved in ether with sodium. The ether had been dried, but not washed before drying, and the small amount of alcohol it contained was enough to convert the whole product into diiododiethoxyquinone, m. 186° (uncor.).

Calc. for $C_6I_2(OC_2H_5)_2O_2$: I, 56.69; found: I, 56.95, 56.40.

Diiododibenzyloxyquinone, $C_6I_2(OC_7H_7)_2O_2$.—Two grams of diiododiphenoxyquinone were treated with the sodium benzylate (made by adding 0.4 g. of sodium to 4 cc. of benzyl alcohol dissolved in 50 cc. of dry benzene; see the preceding paragraph). After heating under a return condenser for 2 hrs. a red solution was obtained mixed with a dark green solid, which we supposed to be principally sodium iodoanilate, because it dissolved in water with the characteristic dark purple color. The residue from the spontaneous evaporation of the benzene solution was freed from benzyl alcohol by washing with a little alcohol, and crystallized from a mixture of benzene and naphtha until it showed the constant m. p. 160° (uncor.).

Subs. 0.1726, 0.2317; AgI, 0.1430, 0.1901.
Calc. for $C_6I_2(OC_7H_7)_2O_2$: I, 44.40; found: I, 44.78, 44.33.

Properties of Diiododibenzyloxyquinone.—It crystallizes in orange-red oblong plates melting at 160° (uncor.). There is no qualitative difference between its solubilities and those of the dimethyl compound. The best solvent for it is naphtha containing a little benzene. Warming with water slowly converts it into iodoanilic acid.

Dibromodibenzyloxyquinone, $C_6Br_2(OC_7H_7)_2O_2$.—Two grams of dibromodiphenoxyquinone were treated with the sodium benzylate (made from 0.4 g. of sodium, 4 cc. of benzyl alcohol and 100 cc. of ether washed till free from alcohol and carefully dried). After heating under a return condenser for an hour the green solid was filtered out. It dissolved in water with the dark purple color characteristic of sodium bromoanilate. The ether was allowed to evaporate spontaneously from the filtrate and the residue, freed from benzyl alcohol by washing with alcohol, was crystallized from naphtha till it showed the constant m. p. 146° (uncor.).

Calc. for $C_6Br_2(OC_7H_7)_2O_2$: Br, 33.44; found: Br, 33.23.

Properties.—It forms orange-red plates, which melt at 146° (uncor.). Its solubilities do not differ qualitatively from those of the corresponding iodo compound, and like that it is saponified slowly by hot water, although unaffected in the cold.

Dibromodiacetoxyquinone, $C_6Br_2(C_2H_3O_2)_2O_2$.—The bromoanilic acid, from which this was prepared, was made by adding to 20 g. of bromoanil 8 g.

of sodium hydroxide dissolved in 125 cc. of water, when, in a short time, the sodium salt separated from the solution, and after dissolving it in the least possible quantity of water, the bromoanilic acid was set free and precipitated by an excess of gaseous hydrochloric acid. Eight grams of the acid were heated with 3 g. of acetic anhydride, until a deep red solution was formed, which, on cooling, deposited yellow crystals. These were washed free of acetic anhydride with dilute alcohol, which, however, saponified a little of the substance, and then crystallized from carbon tetrachloride, till it showed the constant m. p. 205° (uncor.).

Subs. 0.2238, 0.1881; AgBr, 0.2212, 0.1870.

Calc. for $C_6Br_2(C_2H_3O_2)_2O_2$: Br, 41.88; found: Br, 42.07, 42.31.

Properties.—It crystallizes in long, yellow, oblong plates, which melt at 205° (uncor.). It is soluble in alcohol, acetone, ethyl acetate, glacial acetic acid, benzene, or toluene; essentially insoluble in cold ether or naphtha. The best solvent for it is tetrachloride of carbon. It is slowly converted into bromoanilic acid by cold water, quickly by hot water or sodium hydroxide. Its properties, therefore, are analogous in every respect to those of diiododiacetoxyquinone, which has been described in an earlier paper.[1]

Silver Iodoanilate, $C_6I_2(OAg)_2O_2$.—A slight excess of silver nitrate was added to a dilute solution of iodoanilic acid and the red precipitate washed till free from silver nitrate, dried, and warmed with alcohol and benzene when it was dried at 100°. It was analyzed by heating it with fuming nitric acid.

Calc. for $C_6I_2(OAg)_2O_2$: Ag, 35.65; found: Ag, 35.24.

Properties.—It is a dark red amorphous substance insoluble in organic solvents and dilute acids. Even strong nitric acid has no action on it in the cold, but on warming decomposes it with formation of silver iodide.

Diiododiaminoquinone, $C_6I_2(NH_2)_2O_2$.—Two g. of iodoanil were heated with an excess of alcoholic ammonia, and the deep purple product washed first with alcoholic ammonia, later with alcohol, after which it was suspended in a little alcohol, brought into solution with a few drops of sodium hydroxide, and reprecipitated with dilute acid. After this treatment had been repeated several times, it was dried for analysis.

Subs. 0.1994, 0.1806; AgI, 0.2400, 0.2198.

Calc. for $C_6I_2(NH_2)_2O_2$: I, 65.12; found: I, 65.04, 65.79.

Properties.—A brown amorphous solid melting at 230° (uncor.) with evolution of vapors of iodine. It is insoluble in alcohol, acetone, tetrachloride of carbon, glacial acetic acid, benzene, or toluene. A cold solution of sodium hydroxide dissolves it, but it is reprecipitated by dilute acids. When warmed with sodium hydroxide, a small amount of iodoanilic acid is formed.

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[1] THIS JOURNAL, 36, 560 (1914).

Diiododianilinoquinone, $C_6I_2(C_6H_5NH)_2O_2$.—Two grams of diiododiphenoxyquinone were heated with a little more than two molecules of aniline and alcohol, until dark purple needles were forned, which were washed with alcohol, and crystallized 3 times from toluene.

Subs. 0.2347; AgI, 0.2042.
Calc. for $C_6I_2(C_6H_5NH)_2O_2$: I, 46.86; found: I, 47.02.

Properties.—Short, dark purple needles, which begin to decompose at 220°, and melt at 240° (uncor.). If heated with aniline, it forms dianilinoquinone, which was recognized by the absence of halogen, and the characteristic carmine solution formed with strong sulfuric acid. When heated with nitrobenzene the diiododianilinoquinone gives off violet vapors of iodine, which fill the upper part of the flask in a short time. A small quantity of dianilinoquinone was isolated from the product, but no other definite compound could be obtained.

Diiododi-p-toluidinoquinone, $C_6I_2(C_7H_7NH)_2O_2$.—This substance was prepared like the preceding and purified by washing with benzene, alcohol and finally with ether.

Calc. for $C_6I_2(C_7H_7NH)_2O_2$: I, 44.55; found: I, 44.87.

Properties.—It appears in dark purple oblong plates with a metallic reflex, which decompose at 205°, turning black and giving off vapors of iodine. Soluble in nitrobenzene; essentially insoluble in alcohol, ether, acetone, chloroform, tetrachloride of carbon, glacial acetic acid, benzene, or toluene.

Diiodoquinonedimalonic Ester, $C_6I_2(CH(COOC_2H_5)_2)_2O_2$.—Two grams of diiododiphenoxyquinone suspended in 15 cc. of absolute alcohol were treated with the sodium malonic ester (made by adding 0.3 g. of sodium to 20 cc. of absolute alcohol, and after the sodium had disappeared, pouring in 4 g. of malonic ester). The greenish black solution, after standing at ordinary temperatures for 12 hrs., had deposited a blue precipitate of the sodium salt, which was washed with alcohol, in which it is not very soluble, and then dissolved in water. Upon adding dilute acid to the blue solution, a yellow precipitate was formed, which was crystallized from 50% alcohol until it showed the constant m. p. 138° (uncor.).

Subs. 0.2377; AgI, 0.1629.
Calc. for $C_6I_2(CH(COOC_2H_5)_2)_2O_2$: I, 37.58; found: I, 37.04.

The same compound, to judge from its color and that of its salt, was formed when iodoanil was treated with sodium malonic ester, but the yield was small, and the purification much more difficult than when the diphenoxy compound was used. In this respect, the iodine compounds resembled the corresponding chlorine compounds.[1]

Properties of Diiodoquinonedimalonic Ester.—It crystallizes from dilute alcohol in yellow fern-shaped forms and melts at 138° (uncor.). It is

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[1] Jackson, Grindley, *Am. Chem. J.*, 17, 579 (1895).

soluble in alcohol, ether, acetone, tetrachloride of carbon, glacial acetic acid, benzene, or toluene. The best solvent for it is 50% alcohol. A dilute solution of sodium hydroxide forms with it a dark blue solution of the sodium salt, which has an intense blue color, and is very soluble in water, very slightly in alcohol, and insoluble in most of the other organic solvents. Attempts to saponify the ester led to no definite result, as it was carbonized by either sulfuric or hydrochloric acid, as soon as the acid was made strong enough to have any action.

Dibromoquinonedimalonic Ester, $C_6Br_2(CH(COOC_2H_5)_2)_2O_2$.—The sodium malonic ester necessary for 2 g. of the dibromodiphenoxyquinone was made by treating 100 cc. of absolute alcohol with 0.3 g. of sodium and then adding 3 g. of malonic ester. The largest yield was obtained by adding the dibromodiphenoxyquinone in small quantities at a time, and shaking vigorously after each addition. The liquid turned bluish green, and, after standing for 6 hrs., the blue precipitate of the salt was washed with alcohol, dissolved in water, and, after filtering out any unaltered diphenoxy compound, precipitated with dilute sulfuric acid. The orange-brown solution thus obtained usually threw down the free substituted malonic ester after a short time, but, if instead a floating tarry mass was obtained, this solidified more slowly on standing. In either case the product was crystallized from 50% alcohol, until it showed the constant m. p. 109° (uncor.).

Subs. 0.3046; AgBr, 0.2003.

Calc. for $C_6Br_2(CH(COOC_2H_5)_2)_2O_2$: Br, 27.49; found: Br, 27.98.

Properties.—It crystallizes in small yellow needles, which melt at 109° (uncor.). It is easily soluble in alcohol, ether, acetone, chloroform, tetrachloride of carbon, carbon disulfide, ethyl acetate, glacial acetic acid, benzene, toluene, or nitrobenzene. With aniline it forms a dark purple solution, with dimethylaniline a deep blue. Dilute hydrochloric acid, or sulfuric acid, forms a dark brown product, which is mostly carbon; dilute nitric acid converts it into a red oil, which does not dissolve; strong nitric acid dissolves it, and dilution throws down an orange-brown tar, from which we could isolate no definite compound; strong sulfuric acid dissolves it with a dark brown color, from which water throws down a black, highly carbonized precipitate. All our attempts to saponify it were baffled by carbonization.

Dilute sodium hydroxide gives a deep blue solution of the sodium salt, which, in a few minutes, takes on a dark reddish purple color. The addition of an acid now precipitates a brown amorphous substance, and the filtrate gives a test for bromide and for alcohol. This reaction seemed to us so interesting that we spent a long time in attempts to determine its nature, but without result.

Dibromohydroquinonedimalonic Ester, $C_6Br_2(CH(COOC_2H_5)_2)_2(OH)_2$.—

Dibromoquinonedimalonic ester dissolved in toluene was treated with a few drops of phenylhydrazine. Nitrogen was given off and the hydroquinone which was deposited was washed with alcohol and crystallized from toluene until it showed the constant m. p. 183° (uncor.).

Calc. for $C_6Br_2(CH(COOC_2H_5)_2)_2(OH)_2$: Br, 27.39; found: Br, 27.05.

Properties.—It crystallizes in short, white prisms, which melt at 183° (uncor.). It is soluble in alcohol, ether, chloroform, benzene, nitrobenzene, or aniline; essentially insoluble in water, naphtha, or glacial acetic acid. Dilute acids have no action on it; saponification with constant boiling hydrobromic acid gave a brown product, from which we could obtain nothing fit for analysis. A dilute solution of sodium hydroxide forms a light green solution, which gradually changes to dark green, then to purple, and finally to a reddish purple. This final solution is probably identical with the one obtained, when the solution of the sodium salt of dibromoquinonedimalonic ester is allowed to stand. The reddish purple solution deposited a white salt, which dissolved in water and gave a white precipitate with an acid. The salt turned bluish green on exposure to the air. It was not studied further.

Dibromoquinonedibromomalonic Ester, $C_6Br_2(CBr(COOC_2H_5)_2)_2O_2$.—One gram of dibromoquinonedimalonic ester dissolved in 30 cc. of alcohol was treated with 6 to 8 g. of bromine and the mixture heated for half an hour on the water bath under a return condenser. The yellow needles which formed slowly on cooling, were washed with a little cold alcohol and crystallized from hot alcohol until they showed the constant m. p. 172° (uncor.). They were dried *in vacuo*.

Subs. 0.1796, 0.2636; AgBr, 0.1808, 0.2636.

Calc. for $C_6Br_2(CBr(COOC_2H_5)_2)_2O_2$: Br, 43.24; found: Br, 42.84, 42.56.

Properties.—It crystallizes in rosets of small yellow needles, melting at 172° (uncor.), which turn greenish yellow when exposed to the sunlight. It is soluble in acetone, chloroform, ethyl acetate, carbon disulfide, benzene, nitrobenzene, or aniline; very slightly soluble in ether, tetrachloride of carbon, glacial acetic acid, naphtha, toluene, or cold alcohol, soluble in hot alcohol, which is the best solvent for it. Dilute sodium hydroxide gave a reddish brown solution, from which nothing was precipitated on addition of an acid; sodium ethylate, potassium carbonate, or silver oxide gave similar unmanageable results.

When the dibromoquinonedibromomalonic ester was heated with alcohol and bromine for half an hour, yellow needles separated on cooling, which were recognized as dibromoquinonedimalonic ester by the m. p. 108°–109° (uncor.), and the formation of a dark blue solution with sodium hydroxide. The two atoms of bromine in the malonic ester groups may have been replaced by hydrogen by the action of hydrobromic acid, or of the alcohol, or both. If the alcohol causes the reaction, it may explain the low percentages of bromine found in the analyses, since the compound was crystallized from alcohol.

When a few drops of aniline were added to some dibromoquinonedibromomalonic ester dissolved in alcohol, and the mixture heated for several minutes, a purple substance was deposited, which, after washing with alcohol, melted at 175°–180° (uncor.) with such vigorous decomposition that it swelled to three times its original size. It is slightly soluble in acetone, chloroform, ethyl acetate, carbon disulfide, or benzene; essentially insoluble in alcohol, ether, tetrachloride of carbon, glacial acetic acid, naphtha, toluene, or nitrobenzene. It contains no halogen and dissolves in sodium hydroxide solution, forming a purple liquid, from which an acid liberates the original substance. The two bromine atoms in the malonic ester radicals, therefore, have been replaced by hydrogen, and the compound is probably dianilinoquinonedimalonic ester, but, as it lay outside the immediate field of our work, it was not studied in detail.

Tetraiodohydroquinone, $C_6I_4(OH)_2$.—Two grams of iodoanil suspended in 35 cc. of glacial acetic acid were gently warmed and treated with 3 to 5 drops of phenylhydrazine, nitrogen was given off, and the dark brownish purple color changed to light brown, and the hot acetic acid solution after filtration deposited cream colored crystals. Both these crystals and the light brown residue from the glacial acetic acid grew darker on crystallization from glacial acetic acid, undoubtedly owing to the formation of iodoanil, so that the first crystals were probably the purest specimen we obtained.

Calc. for $C_6I_4(OH)_2$: I, 82.74; found: I, 83.41.

Properties.—It was obtained in its preparation as cream colored crystals, which begin to decompose at 238°, and finally melt at 258° (uncor.). On exposure to the air it quickly turns brown from the formation of iodoanil. This tendency to oxidation is so strong that it could not be purified by crystallization in the air. It is soluble in ether, acetone, chloroform, carbon disulfide, or aniline; nearly insoluble in cold alcohol, ethyl acetate, glacial acetic acid, naphtha, benzene, toluene, or nitrobenzene, but dissolves in each of them, when hot, with the exception of naphtha. It dissolves in a boiling solution of sodium hydroxide, and acidification throws down a white precipitate of the hydroquinone.

p-Diacetoxytetraiodobenzene, $C_6I_4(OC_2H_3O)_2$.—Two grams of the tetraiodohydroquinone were thoroughly moistened with acetic anhydride and heated. In the first 20 minutes little or no action was observed, but after half an hour the substance had gone into solution. By adding a little fused sodium acetate the reaction can be made to take place in a few minutes. The hot solution was poured into water and the acetic anhydride destroyed with acid sodium carbonate, after which the product was crystallized 4 times from benzene and dried at 100°.

Calc. for $C_6I_4(OC_2H_3O)_2$: I, 72.78; found: I, 73.11.

Properties.—It forms small white needles, which begin to decompose about 270° and melt at 285° (uncor.). It is slightly soluble in ethyl acetate; practically insoluble in cold alcohol, ether, acetone, chloroform, tetrachloride of carbon, glacial acetic acid, naphtha, benzene, nitrobenzene, or aniline, but soluble in each of these solvents, when hot, with the exception of alcohol and naphtha. Acids, or alkalies, seem to produce no immediate effect on it.

If iodoanil was heated for 10 or 15 minutes with acetic anhydride, the unaltered substance separated on cooling, but, if a few drops of strong sulfuric acid were added, the same length of heating produced a brown solution, which gave a precipitate with water, that after 4 crystallizations from benzene began to darken at 270° and melted at 284° (uncor.). It was therefore the tetraiodo-*p*-diacetoxybenzene.

Action of Chloride of Iodine on Quinone.—Twenty-five grams of chloride of iodine[1] were passed into 15 g. of quinone suspended in 200 cc. of tetrachloride of carbon, and the mixture gently warmed. After the reaction was complete, the precipitate of iodine was filtered out, the filtrate evaporated to dryness, and after removing the iodine by washing with aqueous potassium iodide the yellow residue crystallized from naphtha, until it showed the constant m. p. 161° (uncor.), which indicated that the substance was dichloroquinone, an inference confirmed by the following analyses:

Subs. 0.3284, 0.2167; AgCl, 0.5288, 0.3494.

Calc. for $C_6H_2Cl_2O_2$: Cl, 40.12; found: Cl, 39.81, 39.86.

CAMBRIDGE, MASS.

THE REACTION BETWEEN PHENYL-MAGNESIUM BROMIDE AND UNSATURATED COMPOUNDS THAT CONTAIN A NUMBER OF PHENYL GROUPS.

BY DOROTHY A. HAHN AND RUBY MURRAY.

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A comparison of the results obtained by treating highly phenylated compounds with the Grignard reagent, shows that phenyl groups, in both α and β positions, to carbonyl, effect a much greater hindrance to the reaction than the same number of groups in the α position. Thus, no reaction can be obtained by boiling tetraphenylpropenone[2]

$$(C_6H_5)_2C = C(C_6H_5)COC_6H_5,$$

with phenylmagnesium bromide, while benzpinacoline,

$$(C_6H_5)_3C.COC_6H_5,$$

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[1] Made according to Jackson and Bigelow, *Am. Chem. J.*, 46, 549 (1911).

[2] *Am. Chem. J.*, 38, 519 (1907).