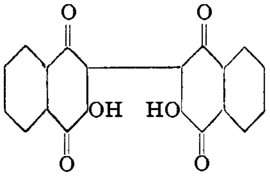
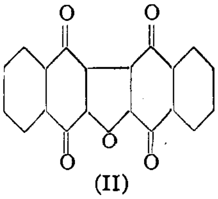
The Action of Light on β-Hydroxy-α-naphthoquinone[1,2]

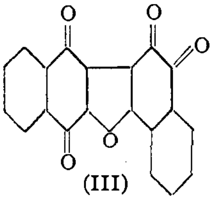
BY SAMUEL C. HOOKER

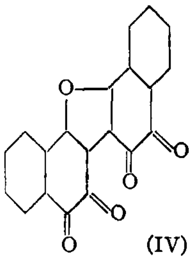
In this paper an account will be given of an interesting substance (I) which was first obtained in the author's laboratory by Mr. J. T. Walsh, Jr., in 1893–1894 from mother liquors in the preparation of 2-hydroxy-1,4-naphthoquinone. It was subsequently established that neutral and acid aqueous solutions in which small quantities of pure hydroxynaphthoquinone are dissolved deposit on standing minute globular masses (dots) of a compound readily distinguished from hydroxynaphthoquinone by the much more crimson color of its solution in alkalies. The substance may be observed floating on the surface of the solution in the course of a few days, or it may not separate for two or three weeks. After standing a number of months, however, unchanged hydroxynaphthoquinone is still present in the solution. The substance is also formed when a small quantity of hydroxynaphthoquinone is dissolved in concentrated sulfuric acid and the acid solution allowed to stand exposed. As water is absorbed crystals of hydroxynaphthoquinone first separate and then eventually give way in part to microscopic globular masses of the condensation product. After observing the phenomenon many times under various conditions it was concluded that the ("dot") compound is formed by the action of light, and as a result of a number of experiments a satisfactory method of preparation was found in exposing an aqueous solution of hydroxynaphthoquinone to ultraviolet light at 70°. The reaction product was obtained in a very good condition in yields of over 40%. When pure it consists of orange-yellow microcrystals melting at 270–275°, dec. It displays various characteristic color reactions and gives a very distinctive pattern when fused on a cover glass and examined under the microscope. Considering the source and acidic character of the material, the composition found for the compound and the observation that it is sparingly soluble in most organic solvents strongly suggested the formula of di-β-hydroxy-α-naphthoquinone, I. A substance regarded as having this structure was prepared many years ago by Chattaway[3] and described as a dark red powder melting at about 215°. Some of the original sample was kindly supplied to the author by Dr. Chattaway in 1922 for purposes of comparison, and it was examined carefully and tested by a number of methods. The material did not appear to be homogeneous, however, and although in some respects it behaved as though it contained the compound described in the present work, attempts to purify the small sample to an extent sufficient to permit a positive identification were not successful.


I

Independent evidence that the oxidation product of hydroxynaphthoquinone has the structure I was found in its behavior under the influence of dehydrating agents. Theoretically a substance of this formula should be capable of yielding in addition to the normal internal anhydride (II) two isomeric anhydrides, III and IV, correspond-


(II)
α,α'-Anhydride


(III)
α,β'-Anhydride


(IV)
β,β'-Anhydride

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(1) See Editor's note (1), THIS JOURNAL, **58**, 1263 (1936).

(2) Following the initial observation of 1893–1894 (see text), Dr. Hooker devoted considerable time in the period 1918–1926 to a study of the formation and properties of the "dot" compound, assisted in part by Dr. G. H. Connitt and by Mr. A. F. Sullivan. Apparently the work was interrupted before it was quite complete, and the observations had been summarized only partially. In repeating some of the experiments in order to comprehend fully the original notes, I was fortunate enough to find a method of preparing in a pure condition the third (red) anhydride, which Dr. Hooker had observed only as an unpurified by-product. The substance was identified by comparison with Dr. Hooker's original, well-preserved slides, and it was thus possible to supply the completing details of the investigation.—L. F. FIESER.

(3) Chattaway, *J. Chem. Soc.*, **67**, 662 (1895).

ing to the conversion of one or both para quinone groups into ortho quinone groups in the course of the dehydration. Analogous changes have been abundantly illustrated in previous work in this Laboratory. Actually it was possible to obtain three such anhydrides, using sulfuric acid as the active dehydrating agent in each case but operating under different conditions. The pure, crystalline compounds are, respectively, orange-yellow, orange and red in color, and although the distinction between the first two is but slight the relationship, in analogy with known cases, is such as to suggest that they have the α,α'-, the α,β'- and the β,β'-structures, in the order named. This was fully confirmed by the behavior of the compounds when boiled with *o*-phenylenediamine in glacial acetic acid solution or suspension. The orange-yellow anhydride, although its solubility in the medium is more than adequate to permit a reaction, was recovered unchanged, as would be expected for the α,α'-quinone II. A mono-azine was obtained from the orange anhydride (III), and the red isomer, in spite of its extremely slight solubility, yielded a diazine (m. p. 409–410°), corresponding to the two β-quinone groups of IV. These observations establish with certainty the structure of the substance formed from 2-hydroxy-1,4-naphthoquinone by the action of light, and it appears that the process involves the oxidative coupling of two molecules at the 3-position.

The occurrence of a second reaction was revealed on investigating the aqueous liquor remaining after removing the main product from the hot solution. This usually deposited in the course of twenty-four hours a brick red crystalline substance amounting to about 15% of the starting material. The material dissolved in 1% alkali to a browner solution than pure hydroxynaphthoquinone, but on exposure on a watch glass the solution soon became lighter in color and eventually corresponded in shade to that of the sodium salt of hydroxynaphthoquinone and on evaporation yielded crystals of this salt. The red color of the substance suggested a β-quinone structure, and its behavior the possibility that the hitherto unknown α-hydroxy-β-naphthoquinone had been discovered. For this reason considerable study was devoted to the matter. By varying the conditions under which the brick red substance was obtained, however, it was found that the color of its alkaline solution was not constant and in some lots this even approached a dark olive green. As the individual crystals of each lot when dusted on the surface of the alkaline solution gave a perfectly uniform color, it seemed probable that the red substance consisted mainly of ordinary hydroxynaphthoquinone modified in its properties by another substance which crystallized with it in varying proportions. This was found to be the case. Starting with 5 g. of the red substance repeated crystallizations from benzene eventually yielded as the less soluble fraction crystals which gave a dark blue solution in alkali. Further purification of these crystals from acetone resulted in their resolution into two substances. The one present in by far the larger quantity dissolved in alkali to a bright blue solution and the other, obtained in exceedingly small amount, gave a dull cherry red solution. The former substance melted at 280°, its blue solution in sodium hydroxide became colorless on exposure, with dilute sodium carbonate a violet solution was obtained, and with concentrated ammonia the substance gave a sparingly soluble, dark violet salt. These properties correspond with those of isonaphthazarin,[4] and a direct comparison with a known sample of this quinone fully established the identity.

Under the influence of light and air in aqueous solution, hydroxynaphthoquinone is partly dehydrogenated and partly hydroxylated, the attack in each case occurring at the free position in the quinone ring.

Experimental Part

Preparation of 2-Hydroxy-1,4-naphthoquinone.—In preparing large quantities of 1,2,4-triacetoxynaphthalene from samples of β-naphthoquinone of various degrees of purity by the method of Thiele and Winter,[5] the crude material precipitated by water was invariably found to contain a by-product which was separated by the following method. The crude material, which varied from orange to brown in color, was boiled with alcohol (10 cc. per gram) until the bulk of the solid had dissolved and the solution was filtered from a small amount of the less soluble by-product. The solution on cooling at first remained clear and deposited heavy crystals of the triacetate. After an hour or so, simultaneously with the commencement of the separation of the by-product, the solution became cloudy and at or before this point the mother liquor was quickly poured off from the heavy crystals. After allowing time for a mixture of the two substances to crystallize from the decanted solution, this was heated to boiling. The triacetate largely dissolved while the second substance passed into solution so slowly that a considerable amount of the material could be collected on filtration. By continuing this process a

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[4] Zincke and Ossenbeck, *Ann.*, **307**, 11 (1899).

[5] Thiele and Winter, *ibid.*, **311**, 345 (1900).

fairly complete separation was possible and the pure triacetate was obtained in about 46% yield from a mixed lot of β-naphthoquinone.

The by-product, which amounted to about one-tenth part of the quinone used, was identified as the tetraacetyl derivative of dinaphthyldihydroquinone by analysis and by direct comparison with a known sample of this substance.[6]

Anal. Calcd. for $C_{28}H_{22}O_8$: C, 69.14; H, 4.56. Found: C, 69.07, 68.92; H, 4.62, 4.80.

On being heated in the capillary tube both samples, as well as the mixture, exhibited the peculiar behavior essentially as described by Straus, Bernoully and Mautner.[7]

For the hydrolysis of the triacetate and oxidation to hydroxynaphthoquinone the following method was found more satisfactory than any described in the literature. A 10-g. portion of the triacetate was immersed in 200 cc. of 5% sodium hydroxide solution in a flat dish and allowed to stand at the laboratory temperature. The solution darkened considerably as the triacetate gradually dissolved and in three to four hours the red sodium salt of hydroxynaphthoquinone commenced to separate. In four to five days the solution became much lighter and cleaner and ultimately approximated in shade that of the sodium salt of pure hydroxynaphthoquinone, indicating that the oxidation was complete. The salt was collected, washed with 5 cc. of water, dissolved in 600 cc. of water at the laboratory temperature, and the filtered solution was acidified, giving a pale yellow crystalline precipitate of hydroxynaphthoquinone in a very pure form and in over 90% of the theoretical yield.

Identification of 2-Hydroxy-1,4-naphthoquinone.—This can be very satisfactorily accomplished with an exceedingly small quantity of the substance even when it is comparatively impure, by first subliming it in a test-tube or on a cover slip. Irregular microscopic yellow crystals are formed, sometimes also needles easily visible to the naked eye. A drop or two of 1% sodium hydroxide is used for dissolving the sublimed crystals and a small portion of the solution allowed to evaporate spontaneously readily yields characteristic red crystals of the sodium salt. To the remainder of the alkaline solution one or more drops of 0.25% hydrochloric acid is added, when with aid of the microscope characteristic needles changing in the course of a few hours to irregular crystals can be observed. The pyridine compound is also characteristic for on evaporation of a drop of the solution in pyridine clusters of bright red needles of the salt are deposited and then the pyridine is spontaneously lost and the crystals lose their red color and their luster but retain their form.

Di-β-hydroxy-α-naphthoquinone (I).—Pulverized hydroxynaphthoquinone (4 g.) was dissolved in 3 liters of boiling tap water and the hot solution was transferred to a 28-cm. crystallizing dish set on a slab of copper heated by a jet burner adjusted to maintain a temperature of about 70°. A Uviarc lamp was so placed that the center of radiation was about 29.2 cm. above the surface of the solution and the exposure was continued for two hours in all. At intervals of thirty minutes three successive 0.5-g. portions of hydroxynaphthoquinone, each dissolved in 400 cc. of boiling water, were added to the main solution, the last addition thus being made thirty minutes before the conclusion of the exposure. Shortly after the commencement of the experiment the compound began to separate on the surface of the solution as a yellow-brown, microcrystalline powder, and at the close of the exposure the substance was immediately filtered off and washed with water. By carefully following the above directions 2.4 g. of di-β-hydroxy-α-naphthoquinone will be obtained in a condition of satisfactory purity. By allowing the temperature to drop materially not only is the action retarded but the compound may be mixed with crystals of hydroxy naphthoquinone. Should this be the case the hydroxynaphthoquinone may be removed by extracting the substance with boiling water (500 cc. per gram).

Di-β-hydroxy-α-naphthoquinone does not dissolve to any appreciable extent in boiling benzene and it is only sparingly soluble in alcohol. The substance dissolves slowly in glacial acetic acid (100 cc. per g.) at the boiling point and the solution on cooling deposits an orange-yellow sandy powder consisting of small crystalline tablets which appear under the microscope to be almost rectangular. The presence of a persistent impurity often gives a brown appearance to the crystals, but this can be removed with the use of blood charcoal. The compound is fairly soluble in nitrobenzene and crystallizes well from this solvent. It is readily soluble in cold pyridine, and it also dissolves in cold dilute alkali and imparts a characteristic, bright crimson color to the solution.

Anal. Calcd. for $C_{20}H_{10}O_6$: C, 69.35; H, 2.91. Found: C, 69.16; H, 3.00.

When heated in a melting point capillary the compound begins to sublime at about 250° and melts with decomposition at about 270–275°. When heated on a cover glass it fuses, simultaneously giving a faint sublimate. When withdrawn from the source of heat the fused material crystallizes to a highly characteristic striated mass of yellow needles frequently suggestive of a map of city streets. The fused material appears to be an anhydride, as it is insoluble in dilute alkali but dissolves slowly on boiling.

α,α'-Anhydride (II).—This compound is the chief product resulting from the action of a mixture of acetic acid and dilute sulfuric acid on di-β-hydroxy-α-naphthoquinone, but it is invariably accompanied by a small amount of the α,β'-anhydride. In preparing the compound the heating should not be prolonged beyond the time necessary to effect the dehydration, as this results in a darker, less pure product. The following method was found most satisfactory. One-half gram of finely powdered di-β-hydroxy-α-naphthoquinone was suspended in 40 cc. of glacial acetic acid and 5 cc. of a solution of equal parts by volume of concentrated sulfuric acid and water, and the mixture was rapidly brought to the boiling point. Within five minutes the starting material had completely passed into solution and in another five minutes the anhydride began to separate. After continuing the boiling for a total of fifteen minutes the mixture was cooled and the crystalline product collected and washed; yield 0.39 g. The material so obtained varies in color from deep golden yellow to dark brown, and it sometimes contains traces of unchanged starting material which can be removed by

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[6] The identification was made by Mr. J. T. Dunn in my laboratory. Microanalyses by Mrs. G. M. Wellwood.—L. F. F.

[7] Straus, Bernoully and Mautner, *Ann.*, **444**, 188 (1925).

digestion with cold 1% alkali. The product was purified by crystallization from glacial acetic acid, using about 230 cc. to the gram and clarifying the solution with animal charcoal. The originally yellow or brown material then acquires a definitely orange cast, the substance separating as well-formed, detached needles of a clear orange-yellow color. The recovery amounted to about 60%, and the mother liquor on spontaneous evaporation deposited first yellowish needles of the same substance, followed by orange tufts of the α,β'-anhydride. After further recrystallization the α,α'-anhydride melted at 349–350°[8] with some decomposition.

Anal. Calcd. for $C_{20}H_8O_5$: C, 73.16; H, 2.46. Found: C, 73.06; H, 2.50.

The substance gives an orange-red solution in concentrated sulfuric acid and the reprecipitated material is pure yellow. The compound was recovered unchanged after being heated for one hour with *o*-phenylenediamine and glacial acetic acid. The anhydride gives a very characteristic fusion test (microscope) strongly resembling that obtained from di-β-hydroxy-α-naphthoquinone. On hydrolysis with boiling alkali the compound is converted into di-β-hydroxy-α-napthoquinone.

α,β'**-Anhydride** (III).—Five grams of di-β-hydroxy-α-naphthoquinone was dissolved in 250 cc. of cold concentrated sulfuric acid and after standing at room temperature for thirty minutes the deep red solution was poured into 3 liters of water. The flocculent orange-red precipitate was washed and dried; yield 4.35 g. This material proved to consist largely of the α,β'-anhydride mixed with a small amount of the red β,β'-isomer. The latter is much the less soluble in organic solvents and its complete removal is not easily accomplished. The α,β'-anhydride can be obtained in a pure condition by repeated crystallization from glacial acetic acid, using each time a quantity of solvent insufficient to dissolve all of the material (250 cc. per gram), but the process is tedious for the β,β'-anhydride dissolves to a very slight but definite extent in acetic acid. A better method was found in the use of dilute (2:1) nitric acid. It was found that the α,β'-anhydride crystallizes very well from the acid while the β,β'-isomer does not appear to dissolve at all in acid of this concentration. When boiled with stronger acid it slowly passes into solution but it apparently is oxidized, for the colorless solution on spontaneous evaporation leaves a residue of colorless crystals. As a result of these tests the following method was adopted. One-tenth gram of the anhydride mixture was added to a mixture of 50 cc. of concentrated nitric acid and 25 cc. of water, heated just below the boiling point. There was a lively evolution of gas and a large part of the material rapidly dissolved. The solution was cooled slightly, filtered through a suitable paper supported by a platinum cone from some undissolved, crimson red material (largely β,β'-anhydride), reheated, and allowed to cool. The α,β'-anhydride crystallized in fine hair-like needles forming a bright orange silky felt. This material was very pure, and the mother liquor yielded a further quantity of equally pure α,β'-anhydride and there was no indication of the presence of the isomer. About half of the weight of the mixture was recovered as pure α,β'-anhydride. Material which had been crystallized twice from glacial acetic acid dissolved nearly completely in the nitric acid solution.

The pure α,β'-anhydride closely resembles the α,α'-isomer in appearance except that it has a brilliant, pure orange color with no suggestion of yellow. It is fairly readily soluble in boiling nitrobenzene and crystallizes as short orange needles. It is more soluble in glacial acetic acid than the α,α'-isomer. The solution in concentrated sulfuric acid is deep red and the reprecipitated material is orange-yellow. The anhydride is slowly attacked by boiling alkali to give a red solution from which di-β-hydroxy-α-naphthoquinone is precipitated on acidification. The α,β'-anhydride melts at 317–318°[8] with some decomposition. It gives a good fusion test.

Anal. Calcd. for $C_{20}H_8O_5$: C, 73.17; H, 2.44. Found: C, 73.28; H, 2.64.

Azine of the α,β'-Anhydride.—One-half gram of the anhydride was dissolved in 200 cc. of glacial acetic acid by boiling and to this was added a filtered solution prepared from 0.6 g. of *o*-phenylenediamine hydrochloride, 2.5 g. of crystalline sodium acetate, and 50 cc. of glacial acetic acid. Heated on the water-bath for forty-five minutes the hot solution deposited yellow crystals of the azine in a good condition, the yield of the washed and dried material being 0.44 g. Crystallized from glacial acetic acid (500 cc.) the substance formed golden yellow plates melting at 329–330°.[8]

Anal.[9] Calcd. for $C_{26}H_{12}O_3N_2$: N, 7.00. Found: N, 6.86.

β,β'**-Anhydride** (IV).[10]—This bright red, sparingly soluble quinone appears to be the sole anhydride formed when di-β-hydroxy-α-naphthoquinone is treated with acetic anhydride in combination with either sulfuric acid or sodium acetate. The substance was satisfactorily prepared by dissolving 0.5 g. of the dihydroxy quinone in 50 cc. of nitrobenzene, cooling the solution to 50°, and adding a solution prepared by dissolving 5 cc. of concentrated sulfuric acid in 20 cc. of acetic anhydride with cooling. The solution became cherry red and almost immediately began to deposit glistening, bright red plates of the β,β'-anhydride. After cooling the material was collected and washed thoroughly with alcohol and benzene; yield 0.43 g. The substance thus obtained was entirely homogeneous and appeared to be directly pure. Recrystallized from nitrobenzene (about 200 cc.) it formed fiery red plates of great beauty.

Anal.[9] Calcd. for $C_{20}H_8O_5$: C, 73.16; H, 2.46. Found: C, 72.68; H, 2.46.

The exceedingly slight solubility of the compound in glacial acetic acid and the action of nitric acid on the substance have been mentioned above. In a capillary tube the anhydride decomposes at about 335–345° without showing signs of melting. When heated on a cover glass and examined microscopically the compound does not seem to melt but strikingly beautiful, deep red scales having a high luster collect on top of the substance heated. When boiled with dilute alkali it becomes green at first, due to a reduction, and then it dissolves to a red solution of the salt of di-β-hydroxy-α-naphthoquinone.

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(8) Determined with a Berl–Kullmann copper block (uncorr.) by L. F. F.

(9) Analysis by Mrs. G. M. Wellwood.

(10) Preparative experiments by L. F. F.

Di-azine of the β,β'-Anhydride.[10]—The anhydride (0.2 g.) was suspended in glacial acetic acid (200 cc.) and refluxed with a solution of *o*-phenylenediamine prepared as above. The red plates were rapidly replaced by hair-like yellow needles of the reaction product, and after refluxing the mixture for two hours the conversion was nearly complete. As microscopic examination revealed the presence of a few unchanged plates of the anhydride, the material was digested for a short time with alkaline hydrosulfite solution containing some alcohol. The unattacked material was crystallized twice from nitrobenzene, in which it is only moderately soluble, clarifying the solution with animal charcoal. The compound was obtained as small, somewhat dull yellow needles, m. p. 409–410°.[8]

Anal.[9] Calcd. for $C_{32}H_{16}ON_4$: N, 11.86. Found: N, 11.70.

Summary

Exposed to the light in aqueous solution, hydroxynaphthoquinone is largely converted into a diquinone by a process of dehydrogenation, and to a lesser extent it is hydroxylated in the quinone ring. A method is described for the preparation of the main reaction product in quantity, and by the isolation of three isomeric internal anhydrides it is established that the substance has the structure of di-β-hydroxy-α-naphthoquinone.

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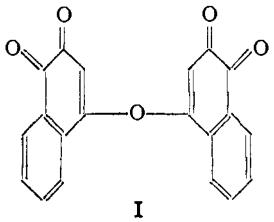
Concerning Wichelhaus' "Di-β-naphthoquinone Oxide"[1,2]

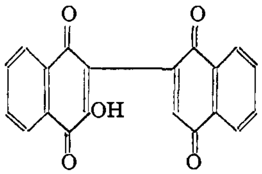
BY SAMUEL C. HOOKER AND LOUIS F. FIESER

In 1897 Wichelhaus[3] discovered that β-naphthoquinone is converted by warm aqueous ferric chloride solution into a substance which evidently is formed from two molecules of the starting material and which Wichelhaus regarded as having the structure of an oxide, I. Although this formula seems inconsistent with Wichelhaus' own observation that the substance dissolves in cold alkali or even soda solution and may be recovered unchanged from the red solutions, the matter does not appear to have received any further attention. On repeating the preparation it was found in the present work that the reaction is very smooth and that the oxidation product can be obtained in a good condition in nearly quantitative yield. The precipitated material first obtained is pure yellow, but it forms orange-red needles when crystallized from acetic acid. That it contains a free hydroxyl group, as suggested by the marked acidic properties, was established by the formation of a monoacetyl derivative. Clearly the oxide structure is inadmissible, and the substance is more properly regarded as a hydroxy dinaphthyldiquinone.



I

The yellow color of the precipitated compound at first suggested the structure of an α-naphthoquinone, and it seemed that the substance could possibly be accounted for by assuming the formation of hydroxynaphthoquinone by oxidation and the condensation of two molecules of this oxidation product with the elimination of water, giving II. This might have been confirmed by the formation of the compound from hydroxynaphthoquinone, but under the above experimental conditions the hydroxyquinone was largely unchanged and yielded none of the condensation product. It was thought also that if the Wichelhaus compound has the structure II it might be expected to yield di-β-hydroxy-α-naphthoqui-



II

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(1) See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

(2) In a letter written to me a few weeks before his death Dr. Hooker commented as follows on a prospective extension of experiments which he had started in 1926–1927 and continued with Dr. G. H. Connitt in 1927–1928 on the structure of the so-called di-β-naphthoquinone oxide: "A number of interesting compounds and reactions resulted from my work with this substance which I shall be glad to see satisfactorily explained." His hope to resume work on the problem was not realized, and the notes which subsequently came to my hand included a formula for the "oxide" which was regarded as purely provisional. The acetyl derivative was described and methods were given for the preparation of the "oxide" and of compounds A, B (first method), C (first method), and D, for the oxidation of A, and for the conversion of D into B, but no formulation was suggested for the new compounds. Following a course which I believe to be in accordance with Dr. Hooker's wishes, I have attempted to carry the work to completion.—L. F. FIESER.

(3) Wichelhaus, *Ber.*, **30**, 2199 (1897).