**Di-azine of the $\beta,\beta'$-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-$\beta$-hydroxy-$\alpha$-naphthoquinone.

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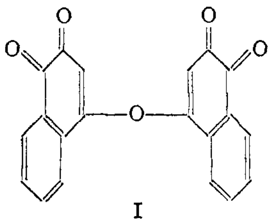
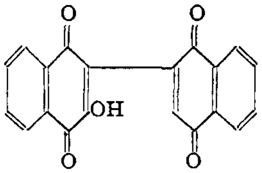
# Concerning Wichelhaus' "Di-$\beta$-naphthoquinone Oxide"[1,2]

BY SAMUEL C. HOOKER AND LOUIS F. FIESER

In 1897 Wichelhaus[3] discovered that $\beta$-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 $\alpha$-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-$\beta$-hydroxy-$\alpha$-naphthoqui-


II

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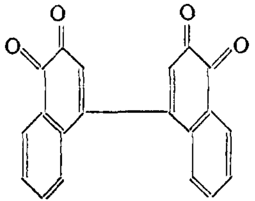
(1) See Editor's note (1), THIS JOURNAL, 58, 1163 (1936).

(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-$\beta$-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).

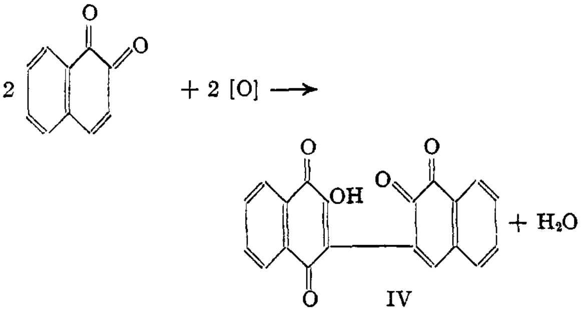
none[4] on oxidation in alkaline solution. This does not seem to be the case, for although oxidation occurs on exposing the alkaline solution to the air the product has quite different properties, as will be described below.

Another hypothesis regarding the formation of the "oxide" was suggested by the observation that on crystallization of the crude product there was isolated a small quantity of the dinaphthyldiquinone III. Although this may arise merely by the oxidation of a trace of dinaphthyldiquinhydrone present in the starting material, it seemed possible that III is an intermediate in the reaction. Experiment showed, however, that the diquinone is practically unchanged even when boiled with aqueous ferric chloride solution. The possibility of the formation of hydroxynaphthoquinone and its immediate condensation with unchanged β-naphthoquinone was similarly eliminated in test experiments, and the problem was then attacked by degradation.



III

On submitting the Wichelhaus compound to zinc dust distillation there was obtained a hydrocarbon which was fully identified as β,β-dinaphthyl by comparison with samples prepared by the zinc dust distillation of di-α-naphthoquinone[5] and by synthesis. Since there is considerable uncertainty in the literature as to the identity of a substance described by Watson Smith[6] as α,β-dinaphthyl, this hydrocarbon was prepared for comparison by synthesis from α-tetralone and β-naphthylmagnesium bromide. The properties of the compound are precisely those reported by Smith and the hydrocarbon is quite different from the above degradation product. The isolation of the β,β-compound provides a significant clue to the structure of the hydroxy dinaphthyldiquinone. Since there is no reason to believe that four of the oxygen atoms do not occupy their original positions in the naphthalene rings, as for example in formula II, and since the pronounced acidity of the compound indicates that the hydroxyl group is situated in a quinone ring, the substance very probably has the structure IV. The presence of a β-quinone group accounts for the orange-red color of the crystalline material, while the color of the alkaline solution is that expected for a β-hydroxy-α-naphthoquinone derivative. The mechanism of the remarkable oxidation reaction is still obscure.



IV

As mentioned above the hydroxy dinaphthyldiquinone is easily oxidized by air in alkaline solution, and an investigation of the reaction product has furnished additional support for the formula IV. The oxidation was accomplished by allowing an alkaline solution of Wichelhaus' compound to go to dryness in an open dish at room temperature, and there was obtained from the residue in over 50% yield a yellow compound ($C_{20}H_{12}O_7$) which gives an orange solution in alkali. This substance, which will be designated A, is quite susceptible to other changes in the presence of acids and bases and even in neutral solvents. In the course of purifying the yellow substance it was discovered that in boiling acetic acid a rather rapid isomerization takes place giving a more stable, yellow compound B which dissolves in alkali with a crimson color. When A is boiled for some time with alcohol it also yields some of the isomer B, but there is formed in addition another yellow compound, C, which differs in composition from the starting material by the elements of carbon dioxide. Compound C can be obtained in good yield by heating A in pyridine with a small amount of copper powder. This decarboxylation clearly shows that the oxidation of the hydroxydinaphthyldiquinone in alkaline solution involves the opening of one of the rings. A similar oxidation can be accomplished with the use of hydrogen peroxide in glacial acetic acid solution, but in this case isomerization also occurs and the product is B.

There are definite indications that the hydroxynaphthoquinone grouping of IV remains intact in the course of the oxidation, one being that on ex-

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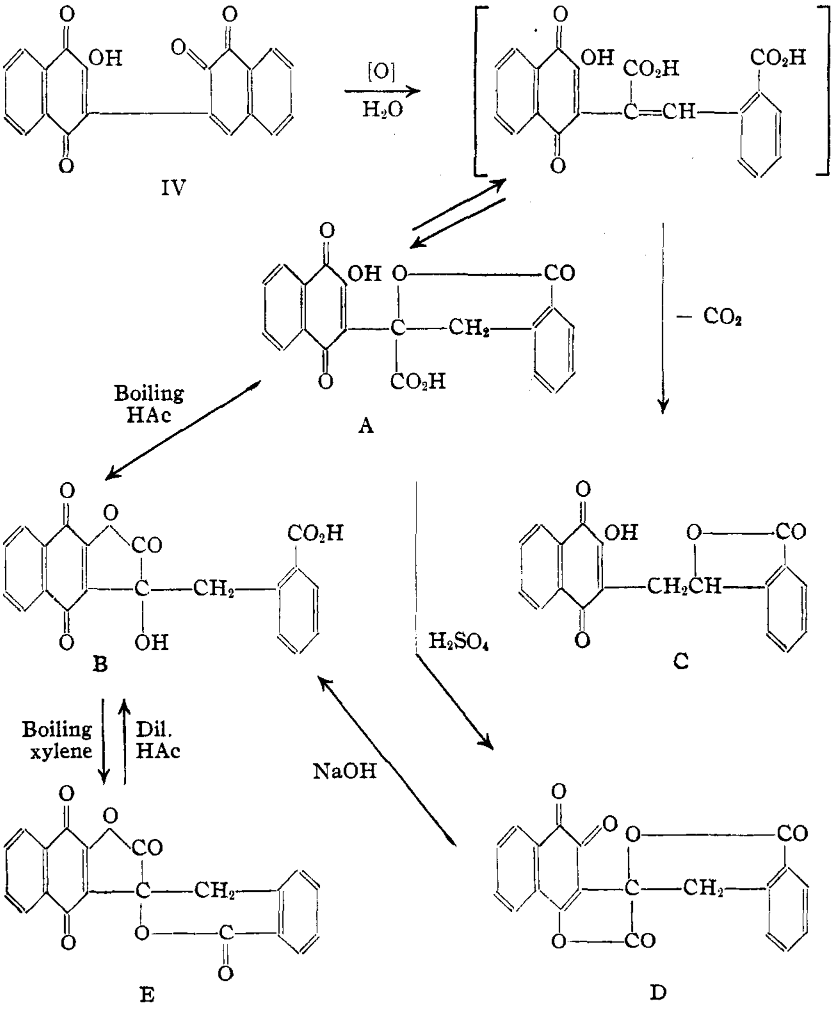
[4] Hooker, THIS JOURNAL, **58**, 1212 (1936).

[5] Witt and Dedichen, *Ber.*, **30**, 2663 (1897).

[6] Smith, *J. Chem. Soc.*, **32**, 560 (1877); **35**, 227 (1879).

posing an alkaline solution of A to the air the substance is converted in part into hydroxynaphthoquinone. The yellow color of compounds A, B and C also suggests the α-quinone structure. By the action of cold, concentrated sulfuric acid A, however, is converted into a red anhydro compound D which appears to be a quinone of the β-series, for it forms a bisulfite addition compound. Dilute alkali converts the substance into B. This interconversion of ortho and para quinone derivatives is likewise indicative of the structure of a hydroxynaphthoquinone.



The facts at present available concerning these and other transformation products suggest a provisional interpretation which is believed to be fundamentally sound if still uncertain in some details. The composition of the oxidation product A is such as to indicate that the reaction involves the rupture of the molecule between two singly linked carbon atoms with the acquisition of two hydroxyl groups. A normal α-diketone oxidation would yield a substance of the formula shown in brackets, but there is evidence that this cannot represent the structure of A. Such a substance probably would be orange or red, because of the unsaturated character of the side chain, and it would surely react with three moles of diazomethane; but A is yellow and yields a dimethyl derivative on treatment with this reagent. The presence in A of but one acidic group in addition to the original hydroxyl group of the quinone ring suggests that the dicarboxylic acid initially formed undergoes lactonization, and for reasons which will be given below compound A is regarded as a δ-lactone of the formula shown. That A is not the primary product is indeed clearly indicated by the color changes observed in carrying out the oxidation. On exposing the alkaline solution of IV to the air it acquires an intensely crimson color as the oxidation proceeds to completion, but the substance (A) which slowly separates after the solution has been acidified dissolves in alkali to an orange, and not a crimson, solution. A satisfactory explanation seems to be that the dibasic acid responsible for the crimson color isomerizes in the acidic solution to the less soluble lactone A. The change seems to be reversible, for on warming the orange alkaline solution of A it acquires a crimson color which persists on cooling.

It seems necessary to assume that A contains a δ- rather than a γ-lactone ring in order to account for the properties of the still more stable isomer B. Only one acidic group is present in B for the substance yields a monomethyl ester on reaction with diazomethane. The ester gives some methane on treatment with methylmagnesium iodide, but apparently other changes obscure the full reaction expected for an alcoholic hydroxyl group. This group seems to be in tertiary combination, for the ester is not acetylated in the presence of either acidic or basic catalysts. This is the chief reason for believing that in the formation of A the lactone ring does not close in the $\gamma$-position, for then B would contain a secondary alcoholic group amenable to acetylation. The properties of B, moreover, are suggestive of a $\delta$- rather than a $\gamma$-hydroxy acid, for it is not very prone to form a dilactone. On boiling a xylene solution of the substance water is easily eliminated giving a yellow anhydro compound (E) which is regarded as a dilactone, but on simply crystallizing the compound from dilute acetic acid it reverts to B with the opening of the second lactone ring. The red compound D is regarded as a dilactone differing from E only in the character of the quinone group, and its ready formation directly from A is understandable in terms of the formulas suggested. According to the above interpretation the isomerization of A to B in acetic acid solution involves the opening of a $\delta$-lactone ring and the closing of a more stable $\gamma$-lactone ring incorporating the acidic hydroxyl group of the quinone.

The ready formation of C in the decarboxylation reaction suggests that the carboxyl group is eliminated not directly from the lactone A but from the unsaturated acid with which A appears to be in equilibrium, particularly in pyridine solution. If an unsaturated hydroxyquinone acid is the immediate product of the decarboxylation it apparently lactonizes at once, for C is yellow, rather than orange-red, and has but one acidic group. The formula suggested for the compound is preferred to that of a dihydrofurano-$\alpha$-naphthoquinone with a free carboxyl group because like other 2-hydroxy-3-alkyl-1,4-naphthoquinones, the compound can be methylated with diazomethane but not with methyl alcohol and a mineral acid. It seems likely that the substance is a $\gamma$-rather than a $\delta$-lactone because it is quite stable and shows no tendency to revert to a hydroxy acid similar to B in aqueous solvents. In cold concentrated sulfuric acid solution C is slowly converted in part into a red anhydro compound F. This was obtained in only very small amounts and it has not been fully characterized, but it does not appear to be an ortho quinone. It is conceivable that the substance is the lactone ($\epsilon$) of an unsaturated hydroxy-$\alpha$-quinone acid, but there is as yet no evidence on this point.

With the possible exception of F the various compounds seem to be satisfactorily accounted for by the formulas suggested and on the basis of the structure IV for the substance resulting from the oxidation of $\beta$-naphthoquinone with ferric chloride. A rigid proof of the individual structures, however, is not available, and the above formulation may require some revision with respect to the exact character of the lactone rings.

## Experimental Part

**2 - Hydroxy - 3,3′ - dinaphthyl - 1,4,1′,2′ - diquinone (IV).**—For the best results in the oxidation the conditions should be controlled more carefully than indicated by Wichelhaus.[3] $\beta$-Naphthoquinone of good quality (10 g.) was finely ground, made into a paste with a part of 400 cc. of water, rinsed into a flask, and treated with 40 g. of ferric chloride crystals dissolved in the rest of the water. The mixture is heated in a water-bath kept at 65–70° and the flask is constantly agitated. The quinone darkens and partly dissolves, and in about one hour the product suddenly becomes uniform brownish-yellow and settles, leaving a clear supernatant solution; the oxidation is then complete. Ordinarily the material is obtained in very satisfactory condition; yield 10.2 g. When the very pure, crystalline $\beta$-naphthoquinone described by Fieser and Fieser[7] is used the grinding of the sample is unnecessary and it is convenient simply to introduce the reagents and provide mechanical stirring. The yield is the same but the product is pure yellow.

For purification the amorphous brown or yellow material was crystallized from glacial acetic acid, using 45 cc. per gram. The first crop (7.7 g.) separated as deep orange-red needles of the best quality. The mother liquor from the crystallization of the brownish-yellow crude material was allowed to stand overnight and a compact orange-red deposit separated. This proved to be almost certainly the dinaphthyldiquinone (III) studied with Walsh,[8] identification being made by means of the color reactions with 1% sodium hydroxide solution.

The pure hydroxydiquinone when introduced to a bath at 230° darkens at about 240° and melts at 253–254° with decomposition. It imparts a bromine color to concentrated sulfuric acid and on absorption of moisture the solution deposits clusters of microcrystals. Water precipitates the unchanged compound as amorphous flocks changing to microcrystalline dots of very characteristic appearance. The compound dissolves easily in dilute alkali in the cold, as well as in sodium carbonate or bicarbonate solution. The solutions are orange-red and became darker when heated. On spontaneous evaporation of a drop of the alkaline solution there appears around it a very characteristic, almost black ring of microcrystals of the sodium salt.

In investigating the formation of the oxidation product the dinaphthyldiquinone III was boiled with strong ferric chloride solution, but it remained unchanged. At 65–70° hydroxynaphthoquinone was attacked to only a minor ex-

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(7) Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

(8) Hooker and Walsh, *J. Chem. Soc.*, **65**, 321 (1894).

tent by aqueous ferric chloride. A mixture of equimolecular amounts of β-naphthoquinone and hydroxynaphthoquinone gave, after recrystallization, no more of the hydroxydiquinone than could be obtained from the β-naphthoquinone used.

The **acetyl derivative of IV** was prepared by slowly stirring 1 g. of the hydroxy compound into a solution of 0.2 cc. of concentrated sulfuric acid in 7 cc. of acetic anhydride at 30–40° for about one hour, a part of the acetate crystallizing during this period. The mixture was poured into water and after several hours the crystalline product (1.1 g.) was collected. The compound is readily soluble in benzene or glacial acetic acid, moderately soluble in alcohol. It crystallizes from methyl alcohol as orange-red prisms or tablets, m. p. 205–205.5°. It is slowly hydrolyzed by 1% sodium hydroxide to the starting material.

*Anal.* Calcd. for $C_{22}H_{12}O_6$: C, 70.96; H, 3.25. Found: C, 70.99, 70.97; H, 2.96, 3.39.

It may be noted that the analysis reported by Wichelhaus[3] for a compound, m. p. 164–165°, which he obtained by reductive acetylation and regarded as a tetraacetyl derivative agrees equally well with the percentages calculated for a pentaacetyl compound.

**Conversion to β,β-Dinaphthyl.**—A finely ground mixture of 2 g. of the hydroxy dinaphthyldiquinone (IV) and 80 g. of zinc dust was placed in a flask, covered with 60 g. of zinc dust, and heated to redness. The distillate, which amounted to about three drops, promptly solidified. The material from three runs was clarified and dried in ether solution, and after taking off most of the ether there was obtained a good yellow solid which was collected and washed with a little ether. After two crystallizations from alcohol it was obtained as thin, iridescent, faintly yellow-green plates, m. p. 180–181°; picrate, m. p. 182–183°.

The zinc dust distillation of di-α-naphthoquinone in the same way gave in similar yield a substance of identical appearance and properties and showing no depression in the melting point. A sample of β,β-dinaphthyl was also prepared by Dr. E. B. Hershberg from β-naphthylmagnesium bromide and β-bromonaphthalene and crystallized from benzene–ligroin. This material was almost colorless (but fluorescent) and melted 1.5–2° higher than the above samples but mixtures of the hydrocarbons and the picrates showed no depression. The synthetic hydrocarbon melted at 185–186°, corr.; picrate, orange-yellow needles from benzene, m. p. 186–187°, corr.

**Synthesis of α,β-Dinaphthyl.**[9]—A solution of 8.8 g. of α-tetralone in absolute ether was slowly added to a solution of the Grignard reagent prepared from 15 g. of β-bromonaphthalene and after refluxing the resulting clear solution for one hour the mixture was worked up in the usual way and the product distilled in vacuum. Vigorous elimination of water occurred at 170–200°, 1–2 g. of naphthalene came over in the fore-run, and the main fraction of unsaturated hydrocarbon distilled at 217–219° (3 mm.) as a yellowish oil; yield 11.3 g. (74%). This material (10.5 g.) was dehydrogenated by heating it with sulfur (1.35 g.) at 230–250° for forty-five minutes and the product was distilled at 2 mm. pressure. The resulting viscous oil slowly solidified and on crystallization there was obtained 9.1 g. of material, m. p. 72–73°. After two recrystallizations the hydrocarbon melted constantly at 74.5–75°, and a sample recovered from the purified picrate melted at the same temperature.

*Anal.*[10] Calcd. for $C_{20}H_{14}$: C, 94.44; H, 5.55. Found: C, 94.52; H, 5.72.

The hydrocarbon crystallizes from petroleum ether in small, ball-like clusters of microcrystals, and the molten material is very slow to solidify. In all of its properties the substance corresponds closely with the compound regarded by Watson Smith[6] as α,β-dinaphthyl (m. p. 76°), and the present results indicate that, contrary to the conclusions of Meyer and Hofmann,[11] Smith was completely successful in isolating the pure hydrocarbon from a mixture consisting chiefly of the two isomers.

The **dipicrate** was best prepared by using two equivalents of picric acid: 4.5 g. of the acid was dissolved in a hot solution of 2.54 g. of α,β-dinaphthyl in 40 cc. of absolute alcohol. The dipicrate which separated on cooling was dissolved with 2 g. of picric acid in 40 cc. of absolute alcohol, and on cooling there was obtained 5.4 g. of heavy, bright orange needles, m. p. 127–127.5°, corr. The melting point was not changed by further crystallization.

*Anal.*[10] Calcd. for $C_{20}H_{14}\cdot 2C_6H_3O_7N_3$: N, 11.80. Found: N, 11.57.

A monopicrate does not appear to be stable, for a solution of equivalent quantities of the components deposited almost exactly the theoretical quantity of the dipicrate and the pure hydrocarbon was recovered from the mother liquor. These observations clearly support the conclusion of Gump[12] that the compound which Wegscheider[13] had in hand was not α,β-dinaphthyl.

**Compound A.**—A solution of 18 g. of 2-hydroxy-3,3′-dinaphthyl-1,4,1′,2′-diquinone in 3600 cc. of 6% sodium hydroxide was distributed amongst six shallow trays of about 645 sq. cm. surface and allowed to evaporate spontaneously in a light room. The at first orange-red solution slowly changed to a permanent crimson. After two weeks the solutions had gone to dryness, and the residues were combined and dissolved in 13.2 liters of water. The intensely crimson alkaline solution was acidified with 480 cc. of concentrated hydrochloric acid made up to a volume of 1200 cc. with water, and the flocculent precipitate which separated immediately was filtered off without delay and discarded (as attempts to purify the material were not successful). The yellow acid filtrate, which should be refiltered quickly in case it is not perfectly clear, was allowed to stand at room temperature for five days, during which time the oxidation product (A) slowly separated as a dull brown-yellow microcrystalline deposit; yield 10.7 g. (54%).

In purifying the crude product care must be taken to avoid prolonged heating of the material in contact with solvents in which it is appreciably soluble (acetic acid or alcohol). One gram of the substance will dissolve in 74 cc. of glacial acetic acid if refluxing is continued for fifteen minutes, but by this time the compound is in part isomerized to B and only 0.22 g. of A separates on cooling. Very

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[9] This experiment was kindly carried out by Dr. E. B. Hershberg.

[10] Analysis by Mrs. G. M. Wellwood.

[11] Meyer and Hofmann, *Monatsh.*, **37**, 710 (1916).

[12] Gump, THIS JOURNAL, **53**, 380 (1931).

[13] Wegscheider, *Monatsh.*, **5**, 238 (1884); *Ber.*, **23**, 3199 (1890).

satisfactory material was obtained by refluxing for two minutes a suspension of 10 g. of the crude oxidation product with 100 cc. of glacial acetic acid, filtering the solution, and washing the undissolved substance with cold glacial acetic acid. The washed material was pure, bright yellow in color and weighed 8.6 g. The wash liquor deposited a crust of brown crystals which can be used for the preparation of B. In recrystallizing A it is not advisable to allow time for complete saturation of the solution. Thus 1 g. of the washed product was added to 75 cc. of boiling glacial acetic acid and after refluxing for three minutes the solution was filtered, leaving a residue of 0.56 g. of undissolved substance. The filtrate was reheated until clear (one minute) and on cooling it deposited 0.20 g. of bright yellow, diamond-shaped plates. Heated in a capillary tube the substance softens at about 201°, runs up the tube with gassing at 203–205°, and then gives a clear yellow liquid. It dissolves in dilute alkali or soda solution in the cold, giving orange solutions which become crimson on warming.

*Anal.* Calcd. for $C_{20}H_{12}O_7$: C, 65.93; H, 3.29. Found: C, 65.50, 65.71; H, 3.53, 3.50.

The **dimethyl derivative of A** was obtained by allowing the substance to stand in contact with an ethereal solution of diazomethane, taken in large excess, for several hours. The acid is sparingly soluble in the medium and it is converted only slowly into the ester, which appears as a less highly colored yellow solid. When nitrogen was no longer evolved the solvent was removed and the residue taken up in glacial acetic acid, in which it is moderately soluble. The solution was diluted at the boiling point with an equal volume of water and after standing at room temperature for several hours it deposited heavy, yellow, prismatic needles. The substance softens at about 220° and melts at 225–226°. It is insoluble in dilute alkali in the cold and hydrolysis occurs slowly at the boiling point, giving a red solution. In the Zerewitinoff test the compound liberated no gas from a Grignard reagent in diphenyl ether–xylene on being heated at 100° for ten minutes.

*Anal.*[10] Calcd. for $C_{20}H_{10}O_5(OCH_3)_2$: $OCH_3$, 15.82. Found: $OCH_3$, 15.74.

**Oxidation of A.**—While compound A can be recovered unchanged from its orange solution in cold 1% alkali if precipitated at once, the solution becomes much darker on standing, and on investigating the material recovered from such a solution after it had been exposed for two days it appeared to contain small amounts of A and B and a positive identification of hydroxynaphthoquinone was made by microscopic tests of the sodium and pyridine salts, the material precipitated from alkaline solution, and the color in sulfuric acid solution.

**Compound B.**—One gram of the substance A was refluxed with 100 cc. of glacial acetic for one and three-quarters hours and the resulting yellow solution was diluted with 100 cc. of hot water. On cooling the pure product slowly separated in the form of rather heavy, flat, yellow needles; yield 0.85 g. The behavior of the substance when heated in a capillary tube is quite characteristic. When introduced to a bath at 200° the material froths vigorously with the liberation of water and then subsides to a dry solid, but when heated gradually in a bath initially at room temperature no change can be detected in the appearance of the crystals as the material is more gently dehydrated. At about 247° minute droplets are formed at the surface of the glass, giving the appearance of orange lines across the tube, and at 264° the substance completely melts to a clear liquid showing some signs of decomposition.

*Anal.* Calcd. for $C_{20}H_{12}O_7$: C, 65.93; H, 3.29. Found: C, 65.85, 66.02; H, 3.48, 3.50.

The compound is stable to the prolonged action of hot glacial acetic acid with or without added hydrochloric acid. It dissolves in cold concentrated sulfuric acid to a light orange-yellow solution from which water precipitates the unchanged compound in an amorphous form rapidly crystallizing to branching curved needles. A drop of the solution exposed on a slide deposits characteristic frondlike clusters and circular groups of crystals. The sulfuric acid solution reddens on warming and then becomes dull brown-red. Compound B dissolves readily in cold 1% sodium hydroxide yielding a crimson solution. On attempting to acetylate B in pyridine solution the material was recovered, after crystallization, in an unchanged condition.

Compound B was also obtained by warming a suspension of 1 g. of the finely powdered hydroxy dinaphthyldiquinone IV in 30 cc. of glacial acetic acid with 1.5 cc. of 30% hydrogen peroxide. After about thirty minutes the material had dissolved to an orange-yellow solution, and this became pure yellow at the end of one hour. The solution was treated with 20 cc. of hot water and on cooling it slowly deposited 0.4 g. of orange-yellow needles. This material was boiled with 15 cc. of glacial acetic acid for one hour, and after adding 7 cc. of water and cooling there was obtained 0.3 g. of yellow needles of B. The substance was identified by the usual tests and by conversion to the ester and the anhydride.

The **methyl ester of B,** prepared as above with diazomethane, crystallized very slowly from a solution in glacial acetic acid which had been diluted at the boiling point with an equal volume of water. It forms flat, pale yellow needles melting at 249–250°, with some previous softening.

*Anal.*[10] Calcd. for $C_{21}H_{14}O_7$: $OCH_3$, 8.20. Found: $OCH_3$, 8.38.

The ester is moderately soluble in glacial acetic acid, sparingly soluble in alcohol or benzene. It is not affected by boiling xylene and crystallizes from this solvent in one or two large, compact clusters of needles. The substance is insoluble in cold alkali but it is hydrolyzed rather readily at the boiling point. It was recovered unchanged after being heated at 100° with acetic anhydride in pyridine solution or in the presence of sulfuric acid. In the Zerewitinoff test 0.1 mole of methane was liberated in the cold and a total of 0.3 mole was evolved after heating at 100° for five minutes.

**Compound E (α-Anhydride of B).**—One-tenth gram of B was brought into solution in 15 cc. of xylene by gentle heating and shaking and the clear yellow solution was boiled for a minute or two on the hot-plate. A ring of moisture appeared and was allowed to escape, and soon the anhydride began to crystallize from the boiling solution as clusters of fine yellow needles. The material collected after cooling amounted to 0.08 g. and it was analyzed without further purification.

*Anal.*[10] Calcd. for $C_{20}H_{10}O_6$: C, 69.36; H, 2.91. Found: C, 69.62; H, 2.95.

Introduced in a capillary tube to a bath at 220° the substance shows no signs of frothing or other change, orange lines appear across the sample at about 249° and melting is complete at 264°. Except for any indication of loss of water, the behavior is identical with that of B, and it is inferred that the latter yields E on being heated without solvent. The anhydro compound is readily soluble in dioxane or tetrachloroethane but does not crystallize well even on the addition of benzene, in which it is sparingly soluble. It dissolves easily in glacial acetic acid and after dilution with hot water the solution deposits needles of B, easily distinguished from the anhydride by the frothing at 200° in a melting point capillary. Compound E dissolves easily in cold alkali or soda solution with a crimson color. On acidifying the cold alkaline solution this turns yellow and cloudy and a small amount of yellow material slowly separates. On boiling this at first dissolves to a clear solution which then deposits a yellow, granular product having the properties of E rather than B (no frothing at 200°). Compounds B and E behave exactly the same in this test and in the tests with sulfuric acid.

**Compound D ($\beta$-Anhydride of B).**—One gram of A was dissolved in 50 cc. of concentrated sulfuric acid at room temperature and after standing for one hour the red solution was poured into 1 liter of water. The flocculent orange-red precipitate was washed and dried (0.98 g.) and crystallized from 25 cc. of glacial acetic acid. The substance forms clusters of red, prismatic blades, m. p. 248–249.5°.

*Anal.* Calcd. for $C_{20}H_{10}O_6$: C, 69.36; H, 2.91. Found: C, 69.10; H, 3.09.

It dissolves slowly in cold sodium bisulfite solution and a colorless addition product separates. Addition of hydrochloric acid to a solution of the colorless material precipitates D. The compound dissolves rapidly in cold 1% sodium hydroxide solution and the yellow material which precipitates on acidification was identified, after crystallization, as B. Reaction occurred on treatment of D with diazomethane and the substance rapidly dissolved in the ether. A glass-like resin was left on evaporating the solvent and it could not be crystallized.

**Compounds C.**—One gram of A was refluxed with 50 cc. of alcohol for five and one-half hours and the resulting solution was allowed to cool and seeded with a crystal of B. After standing overnight 0.16 g. of needles of B deposited. The mother liquor was then evaporated to a volume of 25 cc. and on standing overnight a small additional quantity of B separated. After about ten days a mixture of B and C had crystallized and on warming the solvent in contact with this material the crystals of C dissolved and those of B were filtered off. On standing the mother liquor deposited 0.26 g. of plates of C in a nearly pure condition, m. p. 174–175°.

The substance was obtained in better yield as follows. A solution of 1 g. of A in 15 cc. of pyridine was heated with 0.05 g. of copper powder just at the boiling point for fifteen minutes, when carbon dioxide was no longer evolved, and the red solution was diluted with 100 cc. of water, filtered through a pad of Norite and treated with an excess of hydrochloric acid. The precipitate often carries down some of the pyridine salt, which gives it an orange color, but this can be decomposed by vigorous shaking, giving pure yellow material; yield 0.9 g. Recrystallized from alcohol or alcohol–water the substance formed lustrous yellow plates (0.7 g.) melting at 177.5–178° and giving no depression when mixed with the above sample. It is readily soluble in benzene, alcohol or ether.

*Anal.* Calcd. for $C_{19}H_{12}O_5$: C, 71.24; H, 3.77. Found: C, 71.12; H, 3.93.

The compound dissolves easily in cold dilute alkali (or soda) to a light cherry red solution which does not darken on warming, and the unchanged material is precipitated on acidification. It is not altered by prolonged heating at 100° with a mixture of equal parts of glacial acetic acid and concentrated hydrochloric acid, or by boiling the solution in xylene, or by refluxing for three hours a solution in methyl alcohol containing sulfuric acid.

**Ester of C.**—The reaction with diazomethane proceeds very rapidly and the material all passes into solution. The ester crystallizes very slowly from alcohol, in which it is readily soluble, forming bright yellow, elongated prisms, m. p. 165–166°. It is hydrolyzed slowly by hot 1% sodium hydroxide.

*Anal.*[10] Calcd. for $C_{20}H_{14}O_5$: C, 71.84; H, 4.22; $OCH_3$, 9.28. Found: C, 72.11; H, 4.41; $OCH_3$, 8.85.

**Compound F (Anhydride of C).**—The substance C (0.2 g.) gives a light orange-yellow solution in cold concentrated sulfuric acid (5 cc.) and if the fresh solution is poured into water the unchanged starting material is precipitated. The acid solution darkens on standing and after fifteen hours only a small amount of brown material is precipitated. At intermediate periods C is converted in part into F, as can be seen clearly by observing under the microscope the crystals deposited when a drop of the solution is exposed on a slide, the anhydride forming small rosets of orange-red needles. After three and one-half hours there seemed to be no further increase in the amount of this material and the orange product obtained on precipitation at this point consisted chiefly of unchanged C mixed with about 0.02 g. of the new substance. Being much less soluble in dilute alcohol than C, compound F was easily separated by dissolving the mixture in alcohol and adding water at the boiling point. The substance separated as bundles of hair-like, red needles. It decomposes at about 220–225° and does not dissolve appreciably in cold sodium bisulfite solution.

*Anal.*[10] Calcd. for $C_{19}H_{10}O_4$: C, 75.49; H, 3.34. Found: C, 75.45; H, 3.81.

## Summary

It is shown that the substance obtained by Wichelhaus by the action of ferric chloride on $\beta$-naphthoquinone has the structure of 2-hydroxy-3,3′-dinaphthyl-1,4,1′,2′-diquinone. On exposure of the alkaline solution of the compound to the air for several days a smooth oxidation takes place with the cleavage of the *o*-quinone ring and the formation of an unsaturated hydroxynaphthoquinone dicarboxylic acid derivative which subsequently lactonizes. The resulting substance

has given rise to a number of interesting lactones and dilactones of both the α- and the β-naphthoquinone series and reminiscent of some of the compounds of the lapachol and lomatiol group. These compounds have been investigated and the changes have been for the most part satisfactorily explained.

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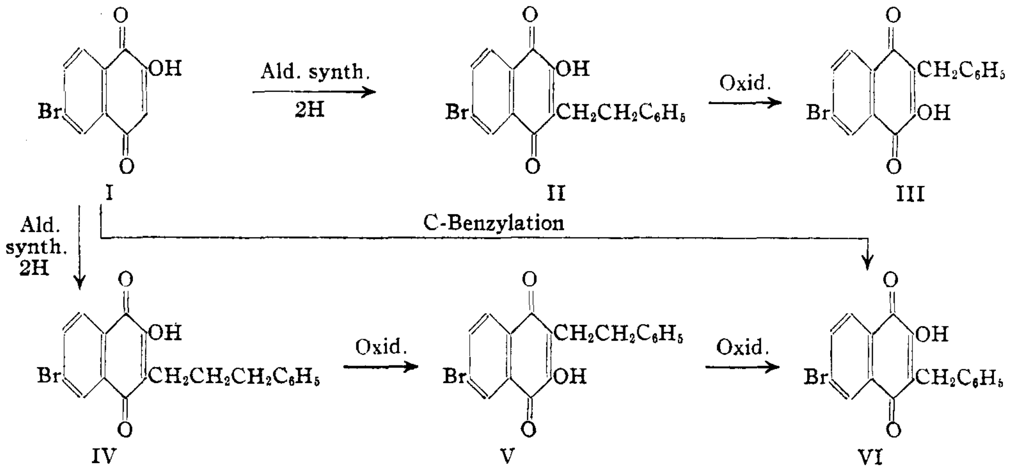
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# Concerning the Mechanism of the Hooker Oxidation

BY L. F. FIESER, J. L. HARTWELL[1] AND A. M. SELIGMAN[1]

In the course of his investigations of the oxidation of alkyl and alkenyl derivatives of hydroxynaphthoquinone,[2] the late Dr. Samuel C. Hooker came to the conclusion that the essential step in the remarkable reaction discovered by him consists in the opening of the quinone ring and its subsequent closing in a different manner, and consequently that the alkyl and hydroxyl groups exchange places as a result of the oxidation. In understanding with Dr. Hooker, and as already mentioned in one of his papers,[2b] we undertook to provide a rigid test of this part of the mechanism by studying the oxidation of naphthoquinones marked with a distinguishing substituent in the aromatic ring.



2-Hydroxy-6-bromo-1,4-naphthoquinone,[3] I, served as a convenient starting material for the preparation of compounds of the type desired, and it was converted into the derivatives II and IV by condensation with the appropriate aldehydes and hydrogenation of the unsaturated side chain of the condensation products, following the general synthetic method of Hooker.[4] Submitted to the Hooker oxidation with alkaline permanganate, the hydrocinnamyl derivative IV yielded a lower homolog isomeric with the synthetic β-phenylethyl compound II but not identical with this substance. The oxidation product therefore has the alternate structure V and the hydroxyl and alkyl groups have assumed new positions with respect to the bromine atom, in accordance with the theory of Hooker. A second oxidation should result in a reversion to the original positions, with the hydroxyl and bromine located at 2 and 6, respectively. That the second oxidation product indeed has the structure VI was established by the independent synthesis of this compound from the silver salt of I by the method of Fieser.[5] According to the theory an isomer of this benzyl derivative should result from the oxidation of the synthetic β-phenylethyl compound II, and this prediction also was verified.

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(1) The work on the bromonaphthoquinones and the experiments in the lapachol series were completed by J. L. Hartwell in 1933; the experiments with the alkylnaphthoquinones were carried out by A. M. Seligman in 1934.

(2) Hooker, THIS JOURNAL, **58** (a) 1168; (b) 1174; Hooker and Steyermark, (c) 1179; (d) 1198 (1936).

(3) Fries and Schimmelschmidt, *Ann.*, **484**, 245 (1930).

(4) Hooker, THIS JOURNAL, **58**, 1163 (1936).

(5) Fieser, *ibid.*, **48**, 3201 (1926).