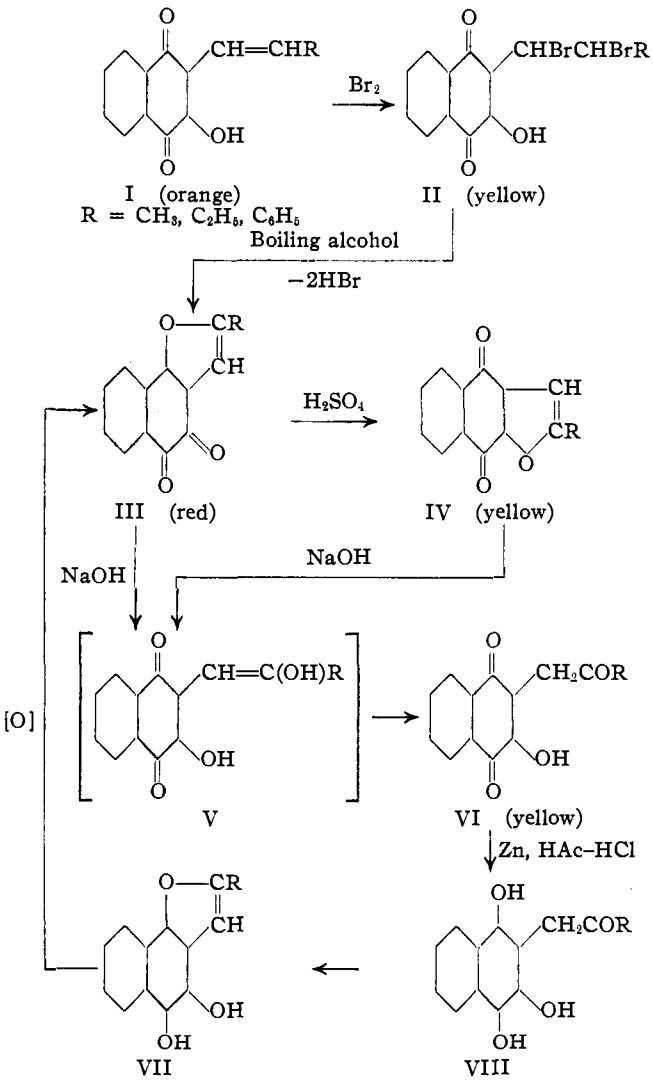
# Conversion of Ortho into Para, and of Para into Ortho Quinone Derivatives. Part IV.[1] Synthesis of Furan Derivatives of α- and β-Naphthoquinones[2,3]

BY SAMUEL C. HOOKER AND AL STEYERMARK

The ready conversion of isolapachol into isopropylfurano-1,4- and 1,2-naphthoquinone was described many years ago in connection with experiments on the structure of lapachol,[4] and the belief was then expressed that the reaction would prove to be a general one. This is abundantly substantiated by the experiments recorded in this paper. The accompanying table shows graphically the formation of the furan derivatives and some of the important reactions studied involving changes from para to ortho quinones and *vice versa*. In some instances the changes take place practically quantitatively, in others modifications occur with the formation of additional substances, but in general the table records the reactions common to the substances examined.




The parent compound of this group of furanonaphthoquinones, IX, was first obtained by Scholl and Zincke[5] from X by a series of changes following the formation of X by alkaline ferricyanide oxidation of alizarin. The furan compound was described as crystallizing in red needles, but in spite of this very characteristic property of ortho naphthoquinones of this type, to which attention has been called repeatedly in former papers,[1a,1b,6] Scholl and Zincke preferred to assign to their compound the formula XI which would be yellow. We shall show that they erred in this respect and that the substance is not a para quinone. In dealing with this subject of quinone change, it may again be emphasized that many compounds are now known of the general formulas XII, XIII and XIV, and that in the course of minor chemical changes of naphthoquinone derivatives *of this type* whenever a red compound passes into a yellow one or *vice versa* it may almost be taken for granted that a change corresponding to this change of color has occurred in the quinone groups.

Errors in the chemical literature have already been corrected[1a,b] where this change in color has been disregarded. There are, however, some known exceptions to the general rule, the causes of which have been fully discussed and explained in recent papers.[7] For instance, in compounds of the type I we have one of these exceptions. These substances, which served as the starting materials for the present syntheses,

(1) Previous papers: (a) Hooker and Carnell, *J. Chem. Soc.*, **65**, 76 (1894); (b) Hooker and Walsh, *ibid.*, **65**, 321 (1894); (c) Hooker and Wilson, *ibid.*, **65**, 717 (1894).

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

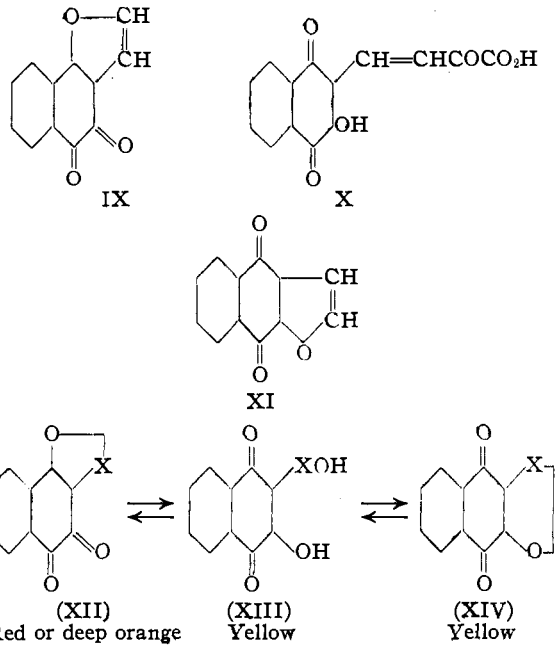
(3) Dr. Hooker wrote the first three paragraphs of this paper and the remainder has been constructed from the notes and reports of the junior author.—L. F. FIESER.

(4) Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).

(5) R. Scholl and A. Zincke, *Ber.*, **52**, 1142 (1919).

(6) Hooker, *J. Chem. Soc.*, **61**, 611 (1892); **63**, 1376 (1893); **65**, 15 (1894); **69**, 1355 (1896); Hooker and Gray, *ibid.*, **63**, 424 (1893).

(7) (a) Hooker, THIS JOURNAL, **58**, 1163; (b) 1168; (c) 1181; (d) Hooker and Steyermark, 1179; (e) 1198 (1936).




were prepared for the most part by the condensation of aldehydes with hydroxynaphthoquinone.[7a] The simplest member of the series, 2-vinyl-3-hydroxy-1,4-naphthoquinone, has not been obtained by this method, possibly because of its unusually sensitive nature, but it has been prepared by the oxidation of the allyl compound.[7d] The compounds in question (I) are not yellow as the para naphthoquinone grouping ordinarily requires, but are deeply colored, usually orange or brick red. This is due to the presence of a double bond in the α,β-position of the side chain. They add bromine readily in chloroform solution forming compounds of the general formula II which with the elimination of the double bond become *yellow*.

The bromine addition compounds (II) are comparatively unstable, being readily converted into furano-1,2-naphthoquinone derivatives, III, which are red. This change takes place gradually with loss of hydrogen bromide even in the dry, purified substances. The bromine compounds can be purified by crystallization from benzene or chloroform but even at ordinary temperatures there is usually slight decomposition. Solution in alcohol containing small amounts of water, sometimes even in the cold, brings about almost quantitative conversion into the corresponding deep red III, due to the passage of the para quinone group of the yellow dibromide into the ortho quinone group of the furan derivative.

In the case of the methyl, ethyl and phenyl derivatives, the red ortho quinones (III) can be isomerized to the yellow para quinones (IV) by the action of sulfuric acid. By boiling the quinones of either type with alkali the furan ring is opened and the same acidic substance is obtained from the two isomers III and IV. Since the resulting compound invariably is *yellow*, the structure must be that of VI, for the unsaturated compound of formula V would be orange or red. The ketonic compounds of the type VI on direct cyclization give mixtures of the ortho and para quinones, but after reduction to the hydroquinones (VIII) ring closure occurs selectively in a single direction and on oxidation the ortho quinones (III) can be obtained in a pure condition.

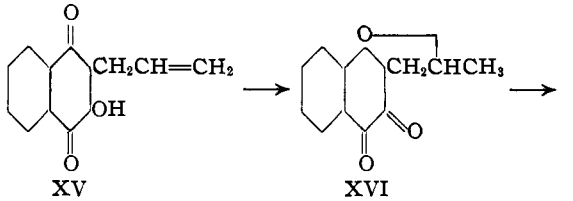
While the methyl and ethyl substituted compounds of the type IV are pure yellow in color and stand in marked contrast to the corresponding red quinones (III) of the ortho series, β-phenylfurano-1,4-naphthoquinone can be obtained both as golden yellow plates and as bright red needles. The red form is the less stable modification and changes into the yellow form when heated. Although it is unusual that a para quinone of this type should exist in any but a yellow condition, even as a metastable form, there is still a considerable contrast between the bright red color of this modification and the dark, purplish-red of the ortho isomer. The latter substance combines with *o*-phenylenediamine to form an azine, and the same characteristic property of an ortho quinone is shared by the methyl and ethyl derivatives, which from their red color alone would be regarded as ortho quinones.

The preparation and characterization of the parent quinone of the furan group presented some difficulties, probably because the general instability of the vinyl derivative of hydroxynaphthoquinone is shared by the other open-chain compounds resulting from it. Only one of the two possible furanonaphthoquinones was isolated, namely, a deep red compound corresponding to the description of Scholl and Zincke. From its color and from the fact that it was obtained by the general method which in other cases leads to the formation of ortho quinones, it can be inferred that the substance is an ortho quinone of the formula IX, a conclusion which is convincingly established by the formation of a characteristic azine in good yield.[8] The quinone is unusually

(8) A further confirmation of the structure is that the substance dissolves in cold sodium bisulfite solution. The action is slower than in the case of the methyl and ethyl derivatives, as might be expected from the much higher melting point of the parent substance, but as with these compounds the quinone is precipitated unchanged on the addition of sodium carbonate.—L. F. F.

stable in concentrated sulfuric acid solution and, although some change occurs after the solution has stood for several weeks, no substance corresponding to a para quinone has been isolated. Attempts to open the furan ring by alkaline hydrolysis indicated that the aldehydic substance first formed undergoes further change in the course of the reaction.

The substituted furanonaphthoquinones of both the ortho and para series are converted by alkalies in good yield into the ketonic compounds of the formula VI. Although the properties of these substances have not been investigated extensively it has been found in one case that the carbonyl group of the side chain is easily reduced by hydrogen in the presence of platinum catalyst, and probably the reaction is a general one. The compound studied was 2-acetonyl-3-hydroxy-1,4-naphthoquinone (R = $CH_3$), and the alcoholic reduction product (XVII) proved to be identical with a substance obtained by Fieser[9] by cyclizing 2-allyl-3-hydroxy-1,4-naphthoquinone (XV) with sulfuric acid and opening the ring by treatment with alkali. The identity of the products verifies




the structures assumed by Fieser for XVI and XVII on the basis of the known rule of addition, and it is of interest that the rule holds for the allyl compound as well as for lapachol[4] although the former substance gives rise to the formation of a five-membered ring while with the latter a six-membered internal anhydride is produced.

## Experimental Part[10]

### Reaction of the Unsaturated Compounds (I) with Bromine

The bromine addition products were prepared by dissolving the unsaturated compound in chloroform (10–20 cc. per gram of material) at room temperature and either quickly treating this with, or adding it to, a solution of somewhat more than one equivalent of bromine in the same solvent (5 cc. per gram). The bromine was absorbed at once, following which the solvent was removed completely, except in the case of the less soluble phenyl compound, by distillation from a water-bath, avoiding unnecessary heating. The residual oil usually crystallized after standing for several hours, and this crude material was quite suitable for use in the next step in the synthesis. The substances were not all obtained in a completely pure condition.

In the case of 2-vinyl-3-hydroxy-1,4-naphthoquinone the chloroform solution of the crude material was filtered from some insoluble residue, cooled to 0°, and poured into the bromine solution. The crude reaction product was very unstable and it was converted at once into the furano-1,2-naphthoquinone. From 1 g. of the 2-$\alpha$-propenyl compound and 0.65 g. of bromine there was obtained, after washing the crystalline reaction mass with 1 cc. of cold benzene to remove adhering resin, 1.5 g. of crude dibromo compound. It crystallized from benzene (5 cc. per gram) as yellow plates, m. p. 156–157°, dec., but the sample decomposed before an analysis could be made.

**2-$\alpha,\beta$-Dibromo-$n$-butyl-3-hydroxy-1,4-naphthoquinone** (II, R = $C_2H_5$) was prepared from 2 g. of the unsaturated compound and 1.3 g. of bromine. Recrystallized from 5 cc. of benzene, the substance formed yellow prisms, m. p. 133–134°; yield, 2.5 g.

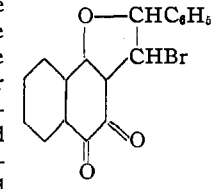
*Anal.* Calcd. for $C_{14}H_{12}O_3Br_2$: C, 43.31; H, 3.11; Br, 41.19. Found: C, 43.60; H, 3.00; Br, 40.51.

**2-$\alpha,\beta$-Dibromo-$\beta$-phenylethyl-3-hydroxy-1,4-naphthoquinone** (II, R = $C_6H_5$).—A solution of 2 g. of 2-$\beta$-phenylvinyl-3-hydroxy-1,4-naphthoquinone in 25 cc. of chloroform was treated gradually at room temperature with 1.6 g. of bromine in 6 cc. of chloroform. After standing one to four days the solution deposited 1.1–1.4 g. of yellow prisms of the addition product, and after concentrating the mother liquor to one-half its volume an additional crop amounting to 0.3–0.4 g. was obtained. A second substance was obtained from the mother liquor as described below. The dibromide was crystallized from chloroform, taking care to avoid undue heating as this results in cyclization to the ortho quinone with the elimination of hydrogen bromide, and the compound was obtained as yellow prisms, m. p. 172.5–173.5°, dec.

*Anal.* Calcd. for $C_{18}H_{12}O_3Br_2$: C, 49.55; H, 2.78; Br, 36.66. Found: C, 49.84; H, 2.92; Br, 37.79, 35.99.

The substance is slowly attacked by concentrated sulfuric acid giving a bluish-green solution; hydrogen bromide is evolved and there is some sulfonation. Cold 1% alkali converts the compound into 2-benzoylmethyl-3-hydroxy-1,4-naphthoquinone, but this is contaminated with other products.

**$\alpha$-Bromo-$\beta$-phenyl-dihydrofurano-1,2-naphthoquinone** was obtained from the mother liquor remaining after the removal of two crops of the dibromide as described above. The substance separated in admixture with some dibromide after further concentration of the chloroform solution. The dibromide was removed by immersion in cold 1% sodium hydroxide solution, and the undissolved material (0.3 g.) was crystallized from alcohol, in which




(9) Fieser, THIS JOURNAL, **48**, 3201 (1926).

(10) Microanalyses by Dr. D. Price of Columbia University.

it is sparingly soluble. The compound first separates as voluminous red needles, which change, on standing in contact with the mother liquor, into dark red plates, m. p. 218–219°. It is readily soluble in benzene or chloroform, it forms an emerald-green solution in concentrated sulfuric acid, and on prolonged boiling with 1% sodium hydroxide it is converted into benzoylmethylhydroxynaphthoquinone, identified by melting point and mixed melting point determinations. During the latter process a part of the material is converted into a greenish-black, alkali-insoluble substance which is oxidized to the starting material by air when in a moist condition.

*Anal.* Calcd. for $C_{18}H_{11}O_3Br$: Br, 22.50. Found: Br, 22.48, 21.80.

**Preparation and Properties of the Ortho Quinones (III)**

**Furano-1,2-naphthoquinone (IX).**—The crude dibromide from 0.4 g. of 2-vinyl-3-hydroxy-1,4-naphthoquinone was dissolved in 25 cc. of cold alcohol and the solution was allowed to stand in the dark in a loosely stoppered flask for one to two months, during which time the solution had evaporated to a volume of about 8 cc. and dark red masses of the reaction product had been deposited. After being washed well with alcohol and dried, the crude material (0.17 g.) was crystallized from alcohol, giving 0.08 g. of product melting at 207°. After two more recrystallizations it was obtained as deep red needles, m. p. 209.5–210°. There was no depression in the melting point when the substance was mixed with a sample prepared by the method of Scholl and Zincke,[5] and both samples gave the identical azine and showed the same behavior in the following test: the solution in concentrated sulfuric acid is blackish-green; on the absorption of moisture from the atmosphere it becomes blue, then purple and finally red needles of the unchanged material are deposited. The substance is more stable in sulfuric acid solution than its homologs, and although some change occurs after the solution has stood for several weeks, a pure transformation product has not been isolated. No change occurred when a solution of the compound in glacial acetic acid was treated with a few drops of concentrated sulfuric acid and boiled for several hours.

The above method of preparation gave better yields than more rapid processes. Thus on boiling the same amount of dibromide with 50 cc. of water for five minutes, filtering the hot solution from resinous material and allowing it to cool, there was deposited 0.015 g. of the quinone, m. p. 206°. The yield was about the same when the dibromide was allowed to stand in contact with water for ten days at room temperature.

**β-Methylfurano-1,2-naphthoquinone** (III, R = $CH_3$) was prepared by refluxing for one-half hour a solution of 1.4 g. of the dibromopropyl derivative in 25 cc. of alcohol. The solution became deep red and on cooling deposited 0.5 g. of red needles of the reaction product. Recrystallized from alcohol the substance formed small red needles melting at 164–164.5°.

*Anal.* Calcd. for $C_{13}H_8O_3$: C, 73.58; H, 3.57. Found: C, 73.44; H, 3.71.

On concentrating the mother liquor remaining after collecting the ortho quinone there was obtained 0.1 g. of the isomeric para quinone. This probably arises from the action of the hydrogen bromide liberated in the reaction on the ortho compound, for the latter substance can be converted in part into the yellow isomer by the action of boiling alcoholic hydrochloric acid.

**β-Ethylfurano-1,2-naphthoquinone** (III, R = $C_2H_5$) was obtained by allowing a solution of 2 g. of the dibromide in 10 cc. of alcohol to stand at room temperature for two days; 0.6 g. of the product crystallized from the solution and 0.8 g. more was obtained on concentration of the mother liquor. The compound forms red needles, m. p. 143.5–144°, from alcohol.

*Anal.* Calcd. for $C_{14}H_{10}O_3$: C, 74.31; H, 4.46. Found: C, 73.97; H, 4.75.

The mother liquor was found to contain a mixture of substances from which cold 1% alkali extracted an acidic compound probably having before hydrolysis the side chain —CH=CBrCH$_2$CH$_3$, for on acidifying the solution the ketonic compound of the type VI was obtained.

**β-Phenylfurano-1,2-naphthoquinone** (III, R = $C_6H_5$). —A solution of 2 g. of the dibromide in 100 cc. of alcohol was refluxed for one and one-half hours, during which time dark red plates of the ortho quinone separated from the boiling solution. After cooling, this material was collected (1.1 g.) and recrystallized from alcohol, in which it is sparingly soluble; dark red plates or needles, m. p. 219.5–220.5°.

*Anal.* Calcd. for $C_{18}H_{10}O_3$: C, 78.81; H, 3.68. Found: C, 78.87; H, 3.74.

The mother liquor yielded a mixture (0.1 g.) of the quinones III and IV with a small amount (0.02 g.) of a substance which could be extracted with cold alkali. The material recovered on acidifying the deep blue filtrate crystallized from alcohol in the form of purple-bronze needles melting with decomposition at about 275°. The substance forms a crystalline, blue sodium salt and gives a purple solution in concentrated sulfuric acid. From the analysis it appears to be a **hydroxyphenylfurano-1,2-naphthoquinone.**

*Anal.* Calcd. for $C_{18}H_{10}O_4$: C, 74.49; H, 3.45. Found: C, 74.04; H, 3.80.

**Azines of the Ortho Quinones.**—These derivatives were obtained in nearly quantitative yield by heating a mixture of the quinone, *o*-phenylenediamine hydrochloride, crystalline sodium acetate and glacial acetic acid at the boiling point for a few minutes. Most of the material separated in a crystalline condition on cooling and the remainder was obtained on dilution. The melting points and analyses of the compounds are recorded in Table I. These azines are all yellow and they crystallize well from alcohol or glacial acetic acid, usually as needles.

TABLE I

AZINES OF FURANO-1,2-NAPHTHOQUINONES

| Substituents | M. p., °C. | %C Calcd. | %C Found | %H Calcd. | %H Found |
|---|---|---|---|---|---|
| None | 195–196 | 79.97 | 79.14 | 3.73 | 4.01 |
| β-Methyl | 209.5–210.5 | 80.25 | 80.26 | 4.26 | 4.19 |
| β-Ethyl | 159–160 | 80.51 | 80.65 | 4.73 | 4.64 |
| β-Phenyl | 237–238 | 83.21 | 83.06 | 4.08 | 3.96 |
| α-Bromo-β-phenyl-α,β-dihydro- | 237–238 | 67.44 | 67.36 | 3.54 | 3.29 |

### The Para Quinones (IV)

The methyl and ethyl derivatives were obtained in quantitative yield by dissolving one part of the ortho quinone in 50 parts by volume of cold concentrated sulfuric acid and allowing the solution to stand at room temperature for twenty-four hours, during which time the initially blue-green solution after passing through intermediate stages became crimson. On pouring the solution into water the yellow product separated in a microcrystalline condition. The compounds crystallize well from alcohol, acetic acid, or benzene. The properties are given in Table II.

TABLE II

FURANO-1,4-NAPHTHOQUINONES

| Substituents | M. p., °C. | Description | % C Calcd. | % C Found | % H Calcd. | % H Found |
|---|---|---|---|---|---|---|
| β-Methyl | 246–247 | Yellow needles | 73.58 | 73.64 | 3.57 | 3.79 |
| β-Ethyl | 145–145.5 | Yellow needles | 74.31 | 74.46 | 4.46 | 5.03 |
| β-Phenyl | 246.5–247.5 | Yellow plates | 78.81 | 78.40 | 3.68 | 3.90 |
| | ..... | Bright red needles | 78.81 | 79.02 | 3.68 | 3.97 |

Since the phenyl derivative of the ortho series is rather easily sulfonated the procedure was in this case modified as follows: 1 g. of the quinone was dissolved in 200 cc. of a mixture of 5 volumes of concentrated sulfuric acid with 1 volume of water, and the solution was heated in a boiling water-bath for one hour. The initially deep blue-green solution gradually became deep violet in color and on pouring the solution into water the product was obtained as a flocculent orange precipitate in about 80% yield. Crystallized from benzene, alcohol, glacial acetic acid or chloroform, the compound separated either as slender, bright red needles or as golden-yellow plates. On standing in contact with the mother liquor for a few days the red variety usually changes into the yellow form. Both forms show the same melting point, for when the red needles are heated at about 195° they soon become yellow while retaining the original form of crystal, and the melting point is that of the yellow modification.

The isomerization of the phenylated ortho quinone can be accomplished also by boiling an acetic acid solution of the substance containing a very small amount of sulfuric acid. The phenylated para quinone dissolves in concentrated sulfuric acid with an intense blue color which slowly changes; the methyl and ethyl compounds give crimson solutions which are more stable. The para quinones sublime readily without charring, while the ortho isomers undergo some decomposition.

The para quinones were obtained in small amounts by allowing solutions of the unsaturated compounds of the type I in concentrated sulfuric acid to stand at room temperature for twenty-four hours, but the yields were poor. No pure product was obtained from the vinyl compound by this method.

### The Ketonic Compounds (VI)

The cleavage of the furan ring of the quinones of both the ortho and para series usually was effected by boiling under the reflux a suspension of one part of the finely powdered material in 100 parts of 1% sodium hydroxide solution until the material had completely dissolved. The phenylfurano-1,2-naphthoquinone is very resistant to attack and in this case the heating was interrupted at two-hour intervals, the solution was filtered, and the residual material, which had become blue as the result of a reduction process, was exposed to the air for re-oxidation and then boiled with a fresh portion of alkali. The isomeric phenylfurano-1,4-naphthoquinone was attacked with still greater difficulty and successive fresh portions of alkali were used; in this case, however, no insoluble blue substance was noticed. The alkaline solutions were orange-brown, and on acidification the reaction product separated as a buff-colored, crystalline precipitate. The pure substances were obtained by crystallization from alcohol or benzene, using animal charcoal. They are all yellow and usually crystallize in the form of needles. The yields, properties and analyses are given in Table III.

TABLE III

KETONIC DERIVATIVES OF 3-HYDROXY-1,4-NAPHTHOQUINONE

| Substituent | M. p., °C. | Time and yield from p-Quinone Hrs. | % | Time and yield from o-Quinone Hrs. | % | % C Calcd. | % C Found | % H Calcd. | % H Found |
|---|---|---|---|---|---|---|---|---|---|
| 2-Acetonyl | 176.5–177.5 | 5 | 71 | 0.5 | 75 | 67.87 | 67.89 | 4.35 | 4.47 |
| 2-γ-Methylacetonyl | 165–165.5 | 3 | 70 | 0.25 | 80 | 68.83 | 68.94 | 4.96 | 5.19 |
| 2-Benzoylmethyl | 182.5–183.5 | 10–12 | 15 | 6 | 70 | 73.94 | 73.73 | 4.14 | 4.32 |

Concentrated sulfuric acid converts these substances first into the ortho furano-1,2-naphthoquinones which then undergo rather rapid transformation into the para isomers. Consequently mixtures of the two compounds are usually obtained on pouring the solutions into water. The orthoquinone can be obtained as the sole product by the method previously[4] used in the lapachol series and indicated in the chart. Thus one part of either of the three compounds listed in Table III was dissolved in 70–100 parts of warm, dilute (55–80%) acetic acid, depending on the solubility, one part of zinc dust was added followed by 16–20 parts of dilute (1:3) hydrochloric acid, and the solution was refluxed for five minutes. Reduction occurred rapidly and the solution of the hydroquinone was filtered to remove the zinc dust, reheated if necessary to bring all of the material into solution, and treated with a solution of 0.25 part of chromic anhydride in 10 parts of water. Red needles of the ortho quinone began to deposit almost immediately, and the material which did not separate on cooling was obtained by diluting the mother liquor. The substances were obtained in practically quantitative yield and in a very pure condition.

**2 - β - Hydroxypropyl - 3 - hydroxy - 1,4 - naphthoquinone (XVII).**—2-Acetonyl-3-hydroxy-1,4-naphthoquinone (0.05 g.) was hydrogenated in alcoholic solution using Adams catalyst, and the solvent was removed from the filtered solution by distillation and evaporation in warm air. The oily residue was taken up in 1% alkali and on acidifying the crimson solution the product separated as a yellow oil which slowly solidified (0.04 g.). Crystallized from benzene or benzene–ligroin the substance melted at 115.5–116.5° and gave no depression when mixed with a sample prepared according to the method of Fieser,[9] although Fieser gave the melting point as 108–110°. In a number of determinations with highly purified samples from both sources the melting point 108–110° was sometimes observed, and after allowing the melt to resolidify

it then melted sharply at 115.5–116.5°. At other times the higher melting point was reached without previous melting. Microscopic examination of the samples prepared by the two methods also indicated their identity. The oil which first separates on acidifying the alkaline solution rapidly crystallizes in the form of very characteristic clusters of yellow needles.


## Summary

The methods developed in 1896 for the synthesis of furan derivatives of β-naphthoquinone, and for the conversion of these substances into the corresponding α-naphthoquinones and open-chain compounds, have been studied in additional cases and found capable of rather general application. The parent compound of this group of furanonaphthoquinones has the ortho quinone structure and is not a para compound as assumed in the literature. The usual relationship between the color and the structure of the quinone group is maintained among the compounds investigated.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RECEIVED APRIL 7, 1936

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# Lomatiol. Part IV. A Violet Quinone from the Oxidation Product[1,2]

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It has been shown[3] that the quinone I resulting from the oxidation of lomatiol easily loses water with the formation of a red ring compound of the formula II. When this is boiled with alkali the pyran ring opens and there is produced a deep crimson solution resembling that formed by the oxidation product I. While I can be recovered without great difficulty by the careful neutralization of its alkaline solutions, the solution prepared from II contains a very unstable hydroxy compound (III) which when in the free condition undergoes cyclization so readily that it has not been possible to isolate the substance. Evidently some change occurs in the side chain of I when the pyran ring is closed and subsequently opened, but it is not known whether the difference is in the spatial arrangement of the groups attached to the double bond, in the respective positions of the hydroxyl group and the double bond in the allylic system, or in other modifications of the original structure. The unstable substance III on liberation from its salts changes into a beautiful, deep violet quinone isomeric with the red anhydride II. The violet compound forms a characteristic azine, indicating the presence of an ortho quinone group, and on catalytic hydrogenation two atoms of hydrogen are added to the unsaturated ring with the formation of the known[3] β-methyldihydropyrano derivative V, and on the basis of these observations the violet substance is assigned the structure of β-methylpyrano-1,2-naphthoquinone, IV.[4]

The new compound differs from the red anhydride II only in the nature of the quinone group, and it is interesting that with this pair of isomers the ortho compound has the deeper color, as in other cases, although on account of the presence of an active double bond in the side ring both quinones are deeper in color than the corresponding naphthoquinones more commonly encountered. The violet ortho quinone (IV) is a highly reactive substance and in aqueous or alcoholic solution it is unstable, particularly in the presence of hydrochloric acid, and undergoes isomerization to the red quinone II. Perhaps it is because of a

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

(2) Although the violet compound was discovered by Dr. Hooker in 1917, most of the experiments described in this paper are of recent date (1934–1935) and no manuscript was left for the paper. At the time of his death Dr. Hooker was undecided as to the exact nature of the key compound and he was uncertain regarding the interpretation to be placed on its various transformations. He thought that a potentiometric analysis might settle the major point of uncertainty, and in a recently completed experiment I have found this to be the case (see footnote 4), although the result is the opposite of that which Dr. Hooker was inclined to anticipate. Seen from this fresh point of view the observations become less puzzling than before, and since I am sure that Dr. Hooker would have modified his early and incomplete views in the light of the later evidence, I have decided to present the theoretical interpretation which appears to be indicated by the facts now available and for which I assume full responsibility. —L. F. FIESER.

(3) Hooker and Steyermark, THIS JOURNAL, **58**, 1198 (1936).

(4) Because of the unusual color of the substance and the peculiar changes occurring in its solutions in acids and bases, and in consideration of early analyses with material later found to be impure, Dr. Hooker at the time of his death was inclined to regard the violet compound as a quinhydrone. He recognized, however, that further evidence was required to settle the matter, and I believe that the following experiment, carried out in my laboratory after his death, provides a sound basis for decision. In an electrode vessel connected to a hydrogen half-cell containing 50% alcoholic 0.1 *N* hydrochloric acid a sample of the substance was introduced to a portion of the same buffer which had been swept free from oxygen by a stream of nitrogen, and the potential was followed from the start. A fairly steady value (0.480 v.) was soon reached and after the material had dissolved a titration with titanous chloride gave a curve of the usual form for a quinone in the completely oxidized condition. The normal potential, $E_0 = 0.435$ v., is consistent with the ortho quinone structure, for it is 70 mv. higher than that of Paternò's dehydrolapachone, a similarly constituted pyrano compound of the para quinone series.—L. F. F.