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

BY SAMUEL C. HOOKER AND AL STEYERMARK

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

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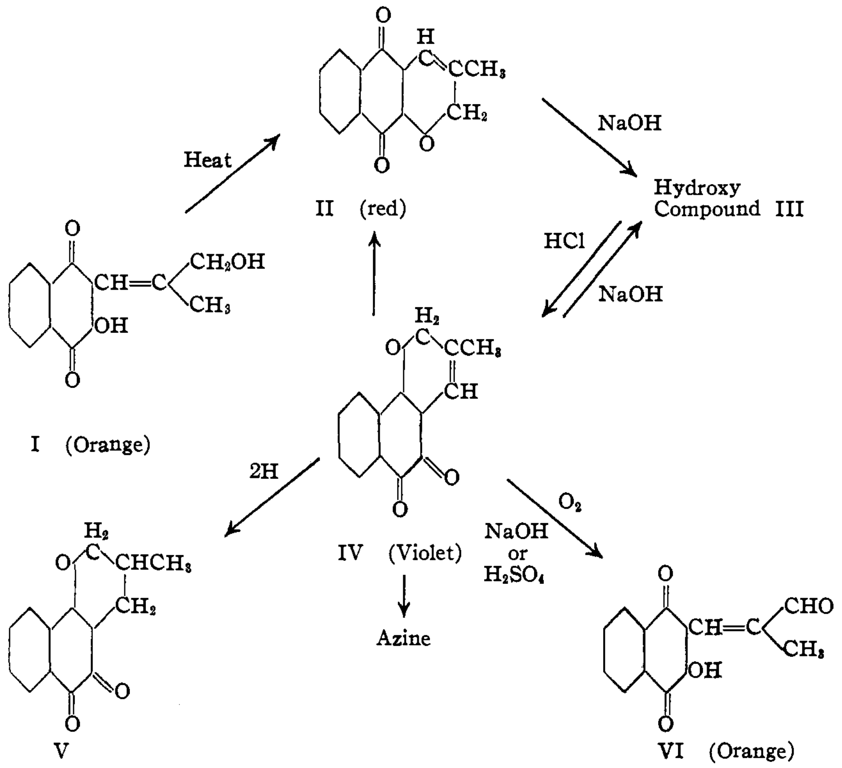
(1) See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

(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.



similar instability that the ortho isomer of Paternò's dehydrolapachone[5] has eluded isolation.

The violet quinone dissolves easily in concentrated sulfuric acid and if the solution is promptly diluted with water the compound is precipitated in an unchanged condition. Likewise, after the quinone has been brought into solution by the action of boiling alkali, the original compound can be recovered if the solution of the hydroxy quinone III is at once acidified. If, however, either solution is allowed to stand for several hours a series of rather remarkable changes occurs which can be summarized briefly as follows. When exposed to the air in an open dish the alkaline solution in a few days deposits red needles of the para quinone II, and the sulfuric acid solution slowly deposits the same substance as it absorbs moisture from the atmosphere. When the freshly prepared solutions are placed in an evacuated system and allowed to stand for some time in the absence of air no red needles are deposited. Changes nevertheless occur under these conditions, for on subsequently exposing the alkaline solution to the air the red compound soon begins to separate and after this material has been removed the alkaline filtrate is found to contain 2-hydroxy-1,4-naphthoquinone, an oxidation product. Under more drastic conditions, as when the alkaline solution is refluxed for several hours, or when air is passed through the solution for a prolonged period, there is produced as a second product of oxidation an orange substance which appears to be an aldehyde of the formula VI. When the sulfuric acid solution of the violet quinone is allowed to stand *in vacuo* for several days and then poured into water, the precipitated material seems to consist largely of the hydroquinone of the orange aldehyde, for when it is dissolved in alkali or in ether in the presence of air there is a rapid color change and the solution is found to contain the aldehydic quinone VI.

The following interpretation of the changes seems to accord with all of the observations. It may be assumed that the pyran ring is opened by sulfuric acid as it is by alkali, and that in any case it is the unknown hydroxy compound III, in the form of the sodium salt or the sulfuric acid ester, which undergoes reaction. The essential change appears to consist in a disproportionation involving the reduction of the quinone group and the oxidation of the side chain. In the early stages of the process the solution contains a considerable amount of the hydroquinone of the hydroxy compound III and this undergoes partial, reversible cyclization to the hydroquinone of the red anhydride II, ring closure occurring more readily with the phenolic reduction product than with the more strongly acidic hydroxy quinone. In the presence of air the hydroquinone is oxidized and the red anhydride is deposited, even from the alkaline solution. In the absence of air the reaction proceeds in the same way at the outset, but when hydroxynaphthoquinone and the aldehyde VI tend to accumulate as oxidation products they are largely reduced by the hydroquinone of the starting material and the latter substance (III) eventually is completely consumed.

The orange aldehyde VI can be obtained in 40–

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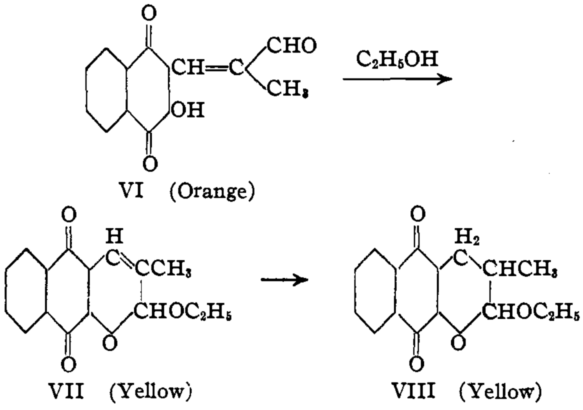
[5] Hooker, THIS JOURNAL, **58**, 1190 (1936).

45% yield by boiling a solution of the violet compound in alkali for several hours, and in this case it is considered that the hydrogen atoms removed from the side chain reduce the quinone group and that the hydroquinone produced throughout the reaction is reoxidized by the air. The structure of the aldehydic substance has not been established rigidly, but the formula suggested accords with the analysis, with the acidic nature of the compound, with evidence indicating the presence of a double bond in the side chain, and with the observation that the substance easily forms derivatives resembling hemiacetals on reaction with various alcohols. In attempting to crystallize the orange compound from methyl, ethyl or butyl alcohol it was found that on mere boiling of the solution a reaction with the alcohol occurs and a yellow, non-acidic product separates on cooling. The reaction products can be reconverted into the starting material by dissolving them in concentrated sulfuric acid or by the action of boiling alkali. The hemiacetal structure VII would account well for the formation of such a compound from VI, for its neutral character, and for its conversion into a dihydro derivative (VIII) on hydrogenation. There is some further support for the hemiacetal structure in the qualitative observation that while the orange compound yields a crystalline, yellow derivative on reaction with aqueous ammonia the alkylated compounds remain unchanged on similar treatment. The yellow color is not easily explained on the basis of this formula, however, for in analogy with the red anhydride II, for which the structure of a pyrano-1,4-naphthoquinone is well established, a compound of the formula VII would be expected to be orange or red, unless the ethoxyl group has an effect opposite to that of the double bond in the side ring. On the other hand, it seems very unlikely that a compound of the formula VI could yield a normal hydroxy quinone ether under the conditions of the experiments or even in the presence of an esterification catalyst. Thus alkyl substituents in the quinone ring of 2-hydroxy-1,4-naphthoquinone effectively hinder a reaction with alcohol and hydrogen chloride, hydrolapachol, for example, being unaffected by such treatment. The hemiacetal formula appears to be the more probable, but further evidence will be required before a final decision can be reached.



VI (Orange)

VII (Yellow)

VIII (Yellow)

For the orange compound the open-chain structure VI is indicated by the fact that the substance dissolves easily in cold alkalies, and the formula is consistent with its color. In organic solvents such as benzene or petroleum ether there may be an equilibrium with a cyclic form. In boiling glacial acetic acid the compound is partially converted into a non-acidic substance having the composition of a bimolecular anhydride. Since such a reaction has not been encountered with other 2-alkyl-3-hydroxy-1,4-naphthoquinones, it seems likely that the elimination of water occurs between two molecules of the cyclic form of the orange compound.

Experimental Part[6]

The Violet Compound: β-Methylpyrano-1,2-naphthoquinone (IV).—It was found convenient to use for the preparation of this compound the crude β-methylpyrano-1,4-naphthoquinone (II) resulting from the oxidation of lomatiol.[3] Five grams of this material was finely ground and boiled with 500 cc. of 1% sodium hydroxide solution for two to four minutes, which sufficed to dissolve the red compound, and the bluish-crimson solution was quickly cooled to room temperature and filtered from about 0.1 g. of the yellow by-product[3] (β-methylfurano-1,4-naphthoquinone). On carefully acidifying the alkaline filtrate there was obtained a yellow emulsion which immediately darkened to violet and began to deposit brownish-violet needles of IV in a fairly pure condition; yield 4–4.5 g. On evaporating the mother liquor to one-tenth its volume, extracting the material which then separated with cold 1% alkali, and crystallizing the extracted substance from alcohol there was obtained about 0.015 g. of a by-product which forms red needles, m. p. 239–240°, dec. (Found: C, 70.52; H, 4.56.)

The violet compound is best purified by crystallization from alcohol, avoiding undue heating of the solution, and it separates either as needles or as diamond-shaped plates of an intense violet color with a somewhat brownish metallic luster, m. p. 156–158°, dec. The substance is also soluble in benzene and in glacial acetic acid, but changes appear to occur when the solutions are boiled.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.31; H, 4.46; mol.

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[6] Microanalyses and molecular weight determinations by Dr. D. Price of Columbia University.

wt., 226.1. Found: C, 74.62; H, 4.62; mol. wt., 238.0, 236.5.

The **azine**, prepared in good yield by heating a solution of the components in glacial acetic acid for a short time, forms gold-yellow needles melting at 163–163.5°. It forms a yellow-green solution in concentrated sulfuric acid and bronze-purple needles of the sulfate separate on dilution.

Anal. Calcd. for $C_{20}H_{14}ON_2$: C, 80.51; H, 4.73. Found: C, 80.34; H, 4.87.

On applying the method[7] found useful for the preparation of other ortho quinones, which in this case consisted in heating the lomatiol oxidation product I with a mixture of zinc dust, hydrochloric and acetic acids, followed by oxidation with chromic acid, there was obtained a mixture of the isomeric violet and red compounds IV and II.

The violet quinone can be converted quantitatively into the red isomer by boiling a solution of the substance in 95% alcohol for four hours, by boiling the material with water for about one hour, or by boiling it with very dilute hydrochloric acid for ten to fifteen minutes. (The violet quinone dissolves easily in cold sodium bisulfite solution, but no precipitate appears when the reagent is neutralized with soda solution.—L. F. F.)

For hydrogenation 0.1 g. of the violet quinone was dissolved in 20 cc. of warm (not boiling) ethyl alcohol and agitated with hydrogen and Adams catalyst for forty-five minutes. The end of the reaction was determined by evaporating a drop of the solution and adding a drop of concentrated sulfuric acid: initial color, blue; final color, red. There was obtained in all 0.07 g. of product which, when recrystallized, was identified by melting point and mixed melting point determinations as β-methyl-dihydropyrano-1,2-naphthoquinone, V.[3]

Action of Alkali on the Violet Compound.—By the action of boiling alkali the violet quinone is soon dissolved, giving a deep red solution. When the solution was at once cooled and neutralized with either hydrochloric acid or carbon dioxide the violet compound was reprecipitated. Allowed to stand exposed at room temperature, the alkaline solution began to deposit red needles of II within two to three days and the amount continued to increase for ten to fourteen days, the total conversion being about 55% of the starting material. During this period a test portion of the alkaline filtrate remaining after the removal of the red needles was shaken with ether, but no color was imparted to the ether layer and consequently the red anhydride was not simply present in solution. The alkaline mother liquor remaining after the final collection of the separated product gave a precipitate of impure 2-hydroxy-1,4-naphthoquinone on acidification. In another experiment the freshly prepared alkaline solution was allowed to stand in a vacuum desiccator, and no red needles appeared after seven days. On then exposing the solution to the air the red anhydride soon separated in 20% yield and the mother liquor yielded a quantity of hydroxynaphthoquinone amounting to about 20% of the weight of the starting material. When air was bubbled through a freshly prepared alkaline solution for fifteen hours and the solution was then allowed to stand in a loosely stoppered flask for three months, none of the red compound was observed but on fractionally precipitating the material in the alkaline solution with dilute acid there was obtained about 15% by weight of the orange compound VI, followed by 65% by weight of hydroxynaphthoquinone, the substances being fully identified by comparison with known samples.

The Orange Compound (VI).—This substance is best prepared by the action of alkali and air on the red anhydride II, the crude material being conveniently employed. A suspension of 1 g. of the powdered substance in 200 cc. of 0.25% sodium hydroxide solution was boiled under the reflux for fifteen minutes and the resulting deep red solution was cooled and filtered to remove the yellow by-product. The refluxing was then continued for a total of seven hours. The brownish-red solution was cooled, filtered from some mineral matter, and acidified. The crude product separated as a buff-colored precipitate which soon became crystalline and from which the sometimes cloudy mother liquor was best removed by decantation. After thorough washing, the crude product was shaken with 100 cc. of cold 0.25% alkali and the resulting solution was quickly filtered and acidified, the material separating as a brownish-orange microcrystalline mass; yield 0.4–0.45 g.

For analysis the substance was crystallized from benzene, in which it is sparingly soluble, and it was obtained in the form of bright orange needles, m. p 229–230°, dec.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13. Found: C, 69.44, 69.24; H, 4.42, 4.06.

The compound gives an orange solution in concentrated sulfuric acid. It dissolves readily in cold dilute alkali giving a crimson solution. When this evaporates on a watch glass the dark red sodium salt is deposited in branch-like forms or as interlacing hair-like needles which begin at the edges of the solution and grow inward. Attempts to obtain an acetate by the action of acetic anhydride or acetyl chloride on the orange compound were unsuccessful. A reaction with ammonia was observed as follows: the orange compound was obtained in a fine suspension by reprecipitation from dilute alkali and in this condition it dissolved at once on adding concentrated ammonium hydroxide solution, giving a deep red solution which soon became yellow and deposited bright yellow needles of a substance melting at 136–137°. Having used filtered solutions, the material was analyzed without further purification with the following results: C, 76.11; H, 4.42; N, 13.02. The compound can be crystallized from benzene or alcohol; it is not soluble in cold alkali but on boiling it yields a light brown-red solution which on cooling deposits nearly colorless needles. The study of the compound was not completed.

Hemiacetals (or Ethers?) of the Orange Compound.—The **ethyl** derivative of the probable formula VII was prepared by refluxing for one and one-half hours a solution of 1 g. of the orange compound in 50 cc. of ethyl alcohol. On cooling about 0.7 g. of the ethyl hemiacetal was deposited in the form of yellow prisms and a further 0.3 g. was obtained on concentrating the solution. The substance is somewhat sparingly soluble in ethyl alcohol and melts at 184.5–185.5°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.18; mol. wt., 270.1. Found: C, 70.72, 70.70; H, 5.09, 5.19; mol. wt., 268.3.

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[7] Hooker, *J. Chem. Soc.*, 69, 1376 (1896).

The compound appears to be partially converted into the methyl derivative on crystallization from methyl alcohol. It is insoluble in dilute alkali in the cold but dissolves slowly on boiling and the orange compound is precipitated when the red alkaline solution is acidified. The hydrolysis is more easily accomplished with the use of alcoholic alkali, followed by dilution with water and acidification. The substance dissolves easily in cold concentrated sulfuric acid and the orange compound precipitates when the solution is poured into water.

The dihydro derivative (VIII) of the ethyl hemiacetal was obtained by hydrogenation of the substance (0.5 g.) in ethyl alcoholic solution (125 cc.) in the usual way; yield, 0.4 g. The reaction product crystallizes slowly but very well from ethyl alcohol, forming yellow crystals melting at 185–186°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.59; H, 5.88; mol. wt., 272.1. Found: C, 70.57; H, 5.35; mol. wt., 279.2.

Although the melting point is nearly the same as that of the unhydrogenated substance, a mixture of the two compounds melted about 20° lower. The dihydro derivative gives a red solution in concentrated sulfuric acid, but in contrast to the starting material water precipitates a mixture of alkali-soluble and alkali-insoluble material.

The *n*-butyl hemiacetal was prepared by refluxing for thirty minutes a solution of 0.2 g. of orange compound in 20 cc. of *n*-butyl alcohol; yield 0.18 g. The substance forms yellow rectangular plates, m. p. 121.5–122°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04; mol. wt., 298.1. Found: C, 72.21; H, 6.31; mol. wt., 292.8.

The **methyl hemiacetal** is similar in properties and melts at 160–161°.

Anhydride of the Orange Compound.—This was obtained by dissolving 1 g. of the material in 70 cc. of glacial acetic acid and refluxing the solution for one-half hour. The reaction proceeds only to the point of an equilibrium, and on cooling the solution deposited 0.7 g. of a mixture of orange needles of the starting material and yellow plates of the anhydride. (A mixture was also obtained on adding water to the mother liquor.) A separation of the two compounds was easily effected by treatment with 70 cc. of cold 0.25% alkali, which rapidly dissolved the orange needles. The solution was quickly filtered and the undissolved yellow plates were washed well with water. By using filtered solutions the anhydride was in this way obtained in a form suitable for analysis, the yield being about 0.1 g. The substance melts with decomposition at 243–244°.

Anal. Calcd. for $C_{28}H_{18}O_7$: C, 72.10; H, 3.86. Found: C, 72.21, 71.79; H, 4.05, 4.11.

The anhydride can be obtained equally well by using propionic or *n*-butyric acid. That an equilibrium is established is shown by the fact that on redissolving the anhydride in any of the solvent acids it is converted into a mixture of the two compounds. The orange compound can be obtained by boiling the anhydride with dilute alkali or by dissolving it in concentrated sulfuric acid and pouring the solution into water.

Action of Sulfuric Acid on the Violet Compound.—The violet quinone gives a deep, rich blue solution in concentrated sulfuric acid, but the color changes to red in one to two hours. When the solution was exposed to the air in an open dish it began to deposit red needles of II within two to three days. The changes occurring in the absence of air are illustrated by the following experiment.

A solution of 1 g. of the violet compound in 100 cc. of concentrated sulfuric acid was allowed to stand in a stoppered flask for two days at room temperature and the solution, which had become red after the first two hours but which deposited no red needles, was poured into 1500 cc. of cold water. The resulting blue-red solution deposited a brown flocculent precipitate which was collected after twenty-four hours and set aside (0.46 g.). On extracting the wine-red filtrate with ether it was noted that on contact with the solvent the aqueous layer generally changed in color from red to yellow and at times orange-yellow microcrystals separated and then dissolved in the ether. It appeared that an oxidation was involved. Evaporation of the ether extract left a residue of yellow crystals mixed with brown resin. On digesting this with 100 cc. of cold 0.25% alkali most of the material quickly dissolved and usually the solution was initially yellow and then rapidly darkened to a crimson color, evidently as the result of the oxidation of a hydroquinone. On filtering the alkaline solution there was a slight residue consisting of yellow plates (0.02 g.) identified as the ethyl hemiacetal of the orange compound, which probably had arisen from reaction with ethyl alcohol present in small amounts in the ether used. After allowing time for oxidation to proceed to completion, the alkaline filtrate on acidification gave a precipitate which was no longer resinous but which consisted of crystalline groups of the orange compound in a nearly pure condition; yield, 0.26 g. Somewhat better yields were obtained in further experiments using less material.

Summary

β-Methylpyrano-1,2-naphthoquinone, a violet colored quinone of a hitherto unknown structural type, has been obtained from the substance resulting from the oxidation of lomatiol. The most interesting and unusual properties of the compound, aside from the striking color, are its ready isomerization to the corresponding para quinone and its conversion, probably through a disproportionation mechanism, into a quinone having an aldehydic side chain. The latter substance also displays novel properties, combining readily with alcohols without the assistance of catalysts, and yielding a bimolecular anhydride.

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