

Periodate Oxidation of Phenols

V*. 2,4-Dimethylphenol

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The action of sodium periodate on 2,4-dimethylphenol produces 2,4-dimethyl-*p*-quinol (II), 2,4-dimethyl-*o*-quinol (III) and 3,5-dimethyl-*o*-quinone (XII). However, of these products, only the *p*-quinol (II) remains unchanged and can be separated from the reaction mixture. The *o*-quinol (III) rapidly dimerises by a Diels-Alder addition to give a 1,4-ethenonaphthalene derivative (IV), and as well gives the yellow *o*-quinol-*o*-quinone adduct (XIII) by diene addition to the *o*-quinone (XII). This adduct can also be obtained as the colourless enol XIV.

Although sodium periodate reacts very slowly with unsubstituted phenol¹, it is rapidly consumed by a variety of alkyl-substituted phenols. In several cases, well-defined reaction products can be isolated**. The present paper deals with the action of periodate on 2,4-dimethylphenol (I).

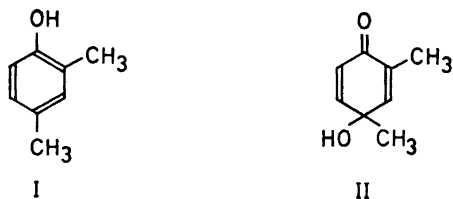
Phenol I when treated in aqueous solution with excess periodate at room temperature consumed slightly more than 1 mole of the oxidant almost instantly; further oxidation after this proceeded very slowly. A methylene chloride extract obtained from the light-red reaction mixture after an oxidation period of a few minutes yielded a crude crystalline product (40%), from which three substances (A, B, C) were separated.

Substance A, m.p. 73—74°, was obtained in a yield of about 2%, based on phenol I, by briefly extracting the crude product with ether. It proved to be identical with 2,4-dimethyl-*p*-quinol (II), which has been described by Bamberger and Brady².

After removing II, the crude product was treated with dilute aqueous sodium hydroxide giving an alkali-insoluble, white residue (substance B) and a deep-yellow solution, which gave a third solid (substance C) on acidifica-

* Part IV: Adler, E., Magnusson, R. and Berggren, B. *Acta Chem. Scand.* 14 (1960) 539.

** Preliminary communication, see Ref. 1⁶



tion. These two products were both obtained in about 20 % yield based on phenol I.

Substance B. Analysis and the molecular weight of the alkali-insoluble substance, m.p. 237—238°, indicated the composition $C_{16}H_{20}O_4$, corresponding to a dimeric oxidation product of I with one extra atom of oxygen per molecule of I. The ultraviolet absorption of B (Fig. 1) showed that the aromatic structure of the starting material (I) had been lost. A strong absorption with a shoulder at 225 $m\mu$ ($\log \epsilon$, 3.88) ("K-band") and a weaker band at 307 $m\mu$ ($\log \epsilon$, 2.48) ("R-band") suggested the presence of an α,β -unsaturated carbonyl grouping. The position of the K-band indicated that the ethylenic bond of this chromophore carried only one substituent (Woodward rules³, *cf.* also Fieser and Fieser⁴); in the present case this substituent would obviously be the ring carbon atom attached to the β -position of the enone grouping. The presence of the latter grouping was also shown by the infrared absorption spectrum (Fig. 2) which had a strong band at 1 680 cm^{-1} (conjugated CO) as well as a weaker absorption at 1 620 cm^{-1} (C = C conjugated with CO). A strong band at 1 720 cm^{-1} indicated the presence of an isolated carbonyl group, and the occurrence of strong absorption in the hydroxyl band region (3 400 cm^{-1}) and the presence of 2 active hydrogen atoms showed that the substance contained

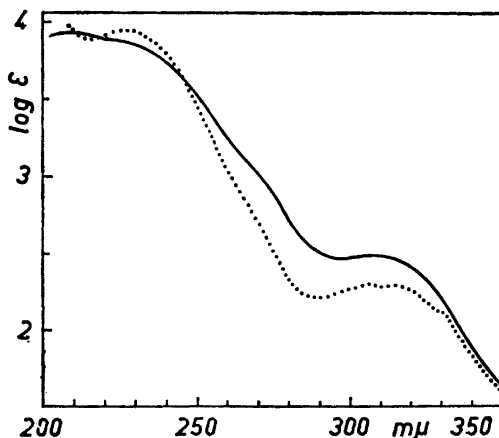


Fig. 1. Ultraviolet absorption spectra. Solvent, 95 % ethanol.
 ————— Dimeric 2,4-dimethyl-*o*-quinol (IV) (= Substance B)
 Diacetate (IV, OAc instead of OH).

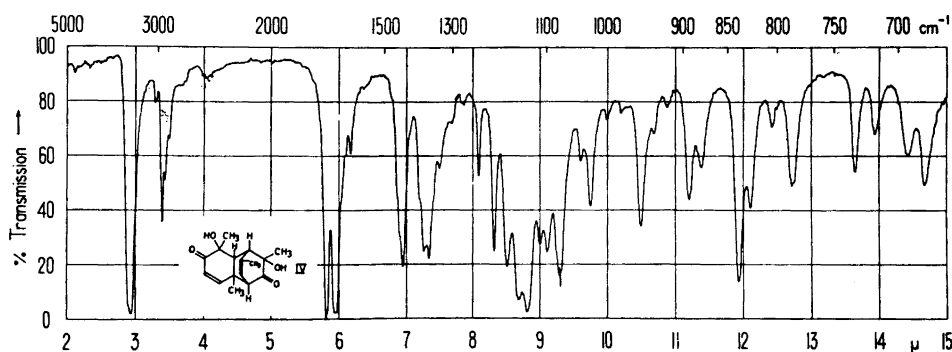
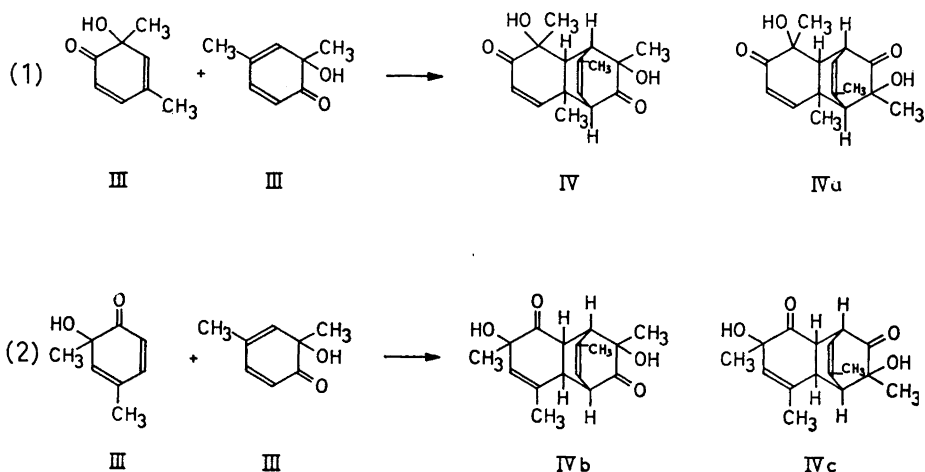


Fig. 2. Infrared spectrum of dimeric 2,4-dimethyl-*o*-quinol (IV) (= Substance B).

two (alcoholic) hydroxyl groups. Although remaining unchanged on refluxing with acetic anhydride-pyridine, substance B gave a diacetate, m.p. 182—184°, in moderate yield when heated with acetic anhydride and sodium acetate, and in good yield when perchloric acid was used as a catalyst. The ultraviolet absorption spectrum of the diacetate (Fig. 1) clearly exhibited the features of an α,β -unsaturated ketone (K-band, λ_{\max} 226 $m\mu$, $\log \epsilon_{\max}$ 3.95). Alkaline hydrolysis of the diacetate regenerated substance B.

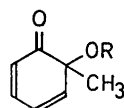
The data reported above suggested that substance B was formed by oxidation of phenol I to a quinol, $C_8H_{10}O_2$, followed by dimerisation. Since the *p*-quinol II is stable in the monomeric form, the intermediate quinol undergoing dimerisation should be the 2,4-dimethyl-*o*-quinol III.

Several *o*-quinones have been found⁵⁻¹⁰ to undergo dimerisation by diene addition. A similar diene reaction between two molecules of 2,4-dimethyl-*o*-quinol (III) could give rise to four isomeric dimers (IVa-c). Isomer IV would

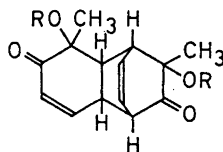


be formed as shown by Scheme (1), the molecule of III acting as a philodiene utilising the γ,δ -double bond of its conjugated carbonyl system. Isomer IVa could be formed in a similar way. The two remaining isomers, IVb and IVc, would be formed by addition of the α,β -ethylenic bond of the philodiene component to the diene system of the second molecule, as shown by Scheme (2). Structures IVb and IVc, however, can be excluded since they do not contain the α,β -unsaturated ketone grouping shown by the ultraviolet and infrared spectra of the substance. Consequently, the neutral dimer, m.p. 237—238° (substance B), could have structures IV or IVa, both of which are in harmony with the experimental data reported above.

No decision between structures IV and IVa has as yet been made, but some evidence in favour of IV is given by a comparison with similar dimeric dienones. Dimerisation by diene addition has recently been found by Metlesics and Wessely¹¹ in the case of 2-methyl-*o*-quinol acetate (V), obtained by oxidation of *o*-cresol with lead tetraacetate. Unlike 2,4-dimethyl-*o*-quinol (III), the *o*-quinol acetate V was stable in the monomeric state at room temperature; it dimerised, however, on heating to 120°¹¹. Hot acid hydrolysis of the result-



V : R = Ac
VI : R = H



VII : R = Ac
VIII : R = H

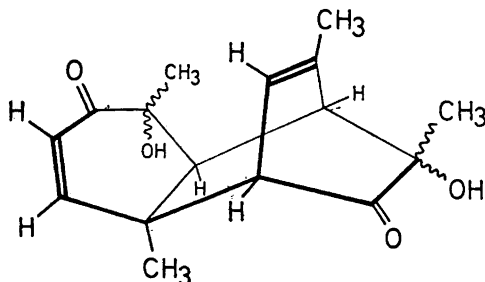
ing dimeric *o*-quinol acetate (VII) gave the dimeric *o*-quinol VIII, which was also obtained on similar hydrolysis of V followed by spontaneous dimerisation of the expected monomeric *o*-quinol VI¹¹. Metlesics and Wessely¹¹ have provided unambiguous proof of structure VIII by degrading the dimer to 1,7-dimethylnaphthalene. On the basis of these results, structure IV, which is analogous to VIII, would seem more probable than structure IVa.

Structure IV rather than the isomeric structure IVa would also be analogous to the structure for dimeric 2,6,6-trimethyl-2,4-*cyclohexadienone* put forward by Brown, Curtin and Fraser¹². The dimerisation of the latter dienone (and of some other cyclic 2,4-dienones reported in literature¹³) is a diene addition quite similar to that occurring with *o*-quinones and *o*-quinols and is subject to similar possibilities of isomerism. In the following, substance B will be assumed to have structure IV although structure IVa cannot be excluded.

The exclusive formation of only one of four possible dimers of the hypothetical *o*-quinol III is a further example of the frequently encountered selectivity of the Diels-Alder reaction. Reaction at the γ,δ -double bond rather than at the α,β -double bond of an $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl system acting as a philodiene has been previously observed^{14,15}.

Assuming that the diene reaction of the *o*-quinol III follows the "endo rule", dimer IV could be given the following steric representation, which is analogous to those proposed by Brown, Curtin and Fraser¹² for dimeric 2,6,6-trimethyl-*cyclohexadienone* and by Metle-

sics and Wessely¹¹ for the dimeric *o*-quinol acetate VII; the configuration at the *tert.* carbinol groups is still unknown.



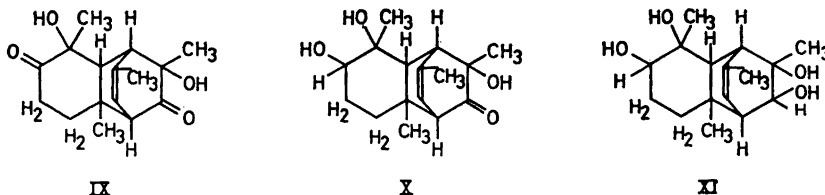
Examination of a Stuart-Briegleb model of IV indicated that the bicyclooctene system present is fairly strained. This may possibly explain the occurrence of the absorption band at $210\text{ m}\mu$ ($\log \epsilon$, 3.93) (see Fig. 1), which might be ascribed to the strained ethylenic bridge.

The formation of dimeric *o*-quinols similar to IV has been observed in this laboratory as a result of the periodate oxidation of other alkylated phenols, including 2,5- and 2,6-dimethylphenol, 2,4,6-trimethylphenol (mesitol) and thymol (preliminary communication, see Ref.¹⁶). In neither case could the expected monomeric *o*-quinol be isolated, since rapid dimerisation took place in the oxidation mixture. Wessely and co-workers^{17,18} obtained 2,3-dimethyl-*o*-quinol and 2,3,5-trimethyl-*o*-quinol as monomers. Recently, periodate oxidation of 2,3,5-trimethylphenol was also found¹⁹ to yield monomeric 2,3,5-trimethyl-*o*-quinol, which does not undergo dimerisation at room temperature. Several monomeric and dimeric *o*-benzoquinols carrying an acetyl residue instead of an alkyl group at the carbinol C-atom of the quinol ring have been obtained in this laboratory by Magnusson²⁰.

The results of some hydrogenation experiments which were carried out with substance B were in harmony with the proposed structure (IV). Hydrogenation, in ethanolic solution, with a Pd-catalyst gave a dihydro derivative, m.p. $194-5^\circ$. It contained two isolated carbonyl groups (infrared absorption bands at 1723 and 1710 cm^{-1}), which indicated that the ethylenic double bond of the conjugated enone system had been hydrogenated. Treatment of IV with hydrogen and platinum oxide in 93 % acetic acid resulted in rapid consumption of 1 mole of H_2 , followed by slow consumption of a second mole. The tetrahydro derivative thus obtained had m.p. $219-20^\circ$ and showed only one carbonyl function in its infrared spectrum. The position of this carbonyl absorption band (1720 cm^{-1}) was similar to that of the unconjugated CO group in the starting material, indicating that, in addition to the ethylenic bond, probably the keto group of the unbridged six-membered ring of IV had been reduced. As a result of the reduction of one of the two keto groups of IV, the infrared spectrum of the tetrahydro compound showed two hydroxyl bands (3500 and 3260 cm^{-1}) as well as a band at 1280 cm^{-1} which can be ascribed to a secondary hydroxyl group. Catalytic hydrogenation of substance B in acetic acid solution over platinum oxide at a pressure of 3.5 atm. produced

a hexahydro derivative, m.p. 201—2°, the infrared spectrum of which was devoid of carbonyl bands but showed strong absorption at $1\ 280\text{ cm}^{-1}$ (*sec.* OH).

On the basis of these results, structures IX, X and XI are proposed for the dihydro, tetrahydro and hexahydro derivatives of IV.



Evidently, hydrogenation of the ethylenic bond of the bridge of the bicyclooctene system did not occur under the experimental conditions used. Another case has recently been reported²¹ in which catalytic hydrogenation of a methyl substituted ethylene bridge, similar to that present in IV, was hindered.

An attempt was made to convert the hexahydro derivative (XI), by heating with selenium, into a naphthalene derivative, which would necessarily involve the elimination of the methyl-substituted ethylene bridge as well as migration or loss of the angular methyl group. However, only small amounts of impure oils could be obtained. The oily products formed on Wolff-Kishner or sodium borohydride reduction of IV also failed to give pure reaction products on distillation at atmospheric pressure or on selenium dehydrogenation.

It is striking that when 2,4-dimethylphenol is treated with excess periodate the dimeric *o*-quinol IV is obtained although the postulated monomeric intermediate (*o*-quinol III) as well as the dimer (IV) contain α -ketol groupings which would be expected to be susceptible to periodate cleavage. However, the isolated dimer IV was found to be practically stable even on several hours' treatment with periodate. It was then expected that the α -glycol groupings present in the hydrogenation products X and XI reported above would be more easily oxidised. In fact, the tetrahydro derivative X consumed 1 mole of periodate in 1 h, further oxidation proceeding extremely slowly, and the hexahydro compound XI consumed 2 moles of periodate in 15 min. These results provide further support of structure IV for substance B and of the structures for its hydrogenation products that are given above. They also exclude the possibility that substance B might be a diene adduct of a mol. of *o*-quinol III, acting as a diene, and a mol. of *p*-quinol II, acting as a philodiene, rather than the dimeric *o*-quinol (IV). Neither of the isomers which could possibly arise by *o*-quinol-*p*-quinol addition would be able to give a hexahydro derivative consuming 2 moles of periodate.

Substance C. When the yellow alkaline extract obtained from the crude periodate oxidation product (*cf.* p. 1261) was poured into excess acetic acid, a colourless substance (C), m.p. 192—193°, precipitated. It had the composition $\text{C}_{16}\text{H}_{18}\text{O}_4$ with two hydrogen atoms less than the neutral product B (IV). The acidic character of C is due to the presence of an enolic hydroxyl group; this was indicated by the intense (dark violet-brown) colour reaction with ferric chloride. Absorption at $1\ 634$ and $1\ 715\text{ cm}^{-1}$ in the infrared spectrum

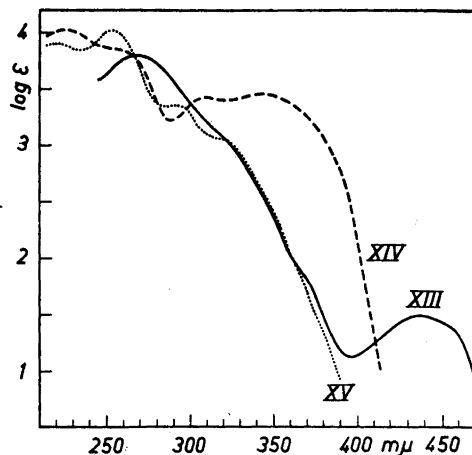
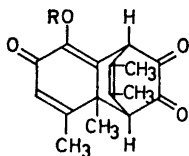


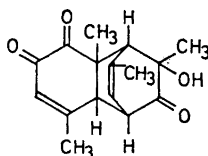
Fig. 4. Ultraviolet absorption spectra. Adduct of 2,4-dimethyl-*o*-quinol and 3,5-dimethyl-*o*-quinone (= Substance C),
 ————— keto form (XIII); solvent, chloroform
 - - - - - enol form (XIV); solvent, 95 % ethanol
 monoacetate of enol form (XV); solvent, 95 % ethanol.

in the postulated structure XIV. Furthermore, substance C when treated with acetic anhydride-pyridine gave a monoacetate (XV), m.p. 213—214°, the ultraviolet absorption of which (Fig. 4) again was very similar to that of the monoacetate (XVII) of the enol XVI of Horner and Sturm.

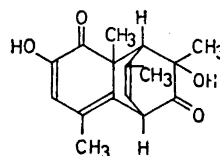


XVI : R = H

XVII : R = Ac



XVIII

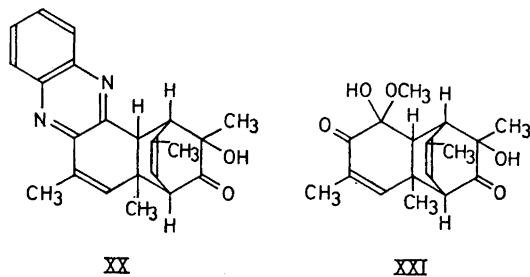


XIX

Since the *o*-quinone XII is unsymmetrically substituted, and either of its two C=C double bonds might be expected to have philodienic properties, a Diels-Alder addition of XII and III could alternatively yield the adduct XVIII, isomeric with XIII. The enol form of XVIII, *i. e.* XIX, however would have a 2-hydroxy-2,4-dienone chromophore rather than the "crossed conjugated" 2-hydroxy-2,5-dienone system present in Horner and Sturm's enol (XVI) and therefore almost certainly would have an ultraviolet absorption markedly different from that of the latter enol. This seems to exclude structure XIX for the enol C.

As mentioned above, the colourless enol XIV is precipitated from its yellow solution in aqueous alkali by pouring the solution into an excess of acetic acid. Slow neutralisation of the alkaline solution with acetic acid, however, produced

a yellow crystalline product, which after recrystallisation from ethyl acetate had a melting point (193—194°) only a few degrees above that of enol XIV; unlike the colourless enol, the yellow product gave no colour reaction with ferric chloride. The infrared spectrum of the yellow substance (Fig. 3a) showed three carbonyl bands (1 724, 1 704 and 1 662 cm^{-1}) instead of the two carbonyl bands for enol XIV; a further band at 1 630 cm^{-1} can be ascribed to an ethylenic bond conjugated with a CO group. The ultraviolet spectrum (Fig. 4) has a maximum at 269 $\text{m}\mu$ ($\log \epsilon$, 3.80) and in addition, a weak absorption band with a maximum at 437 $\text{m}\mu$ ($\log \epsilon$, 1.48) which indicates the presence of a 1,2-diketone grouping and is responsible for the yellow colour of the substance. The formation of a quinoxaline derivative (XX), m.p. 161—162°, on treatment with *o*-phenylenediamine confirms the occurrence of a 1,2-diketo grouping. Like enol XIV, the yellow substance dissolves in aqueous alkali yielding an intensely yellow solution (enolate of XIV) from which either the colourless enol XIV or the yellow substance (or mixtures of both) can be recovered depending on the manner, in which neutralisation is carried out (see above). Treatment of the yellow product with acetic anhydride-pyridine gave the enol acetate XV. From these results it is evident that the yellow product is the keto form XIII of substance C, and that the enol form XIV and keto form XIII are interconvertible.

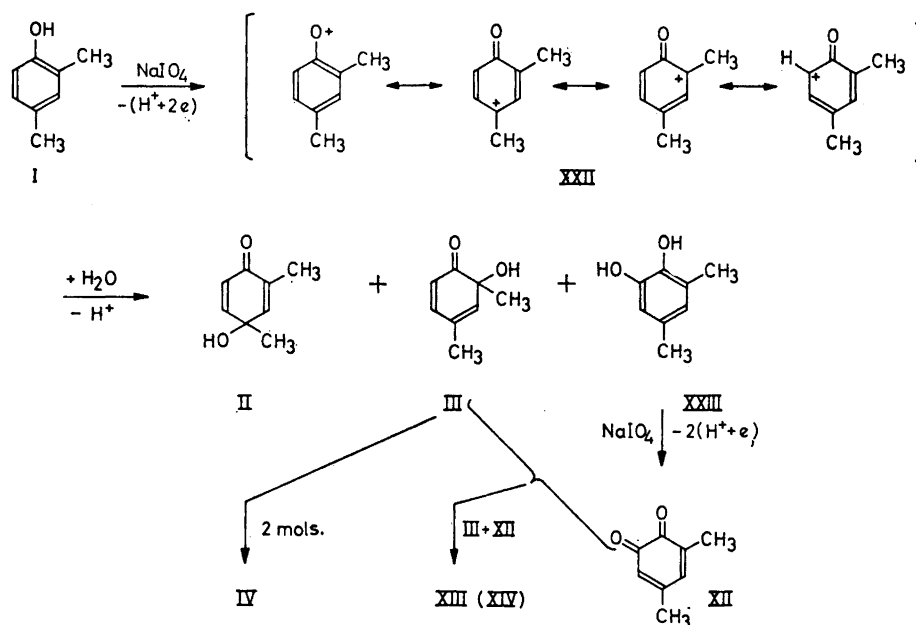


Recrystallisation of ketone XIII from methanol gave a colourless substance, the m.p. (191—192°) of which was approximately the same as that of XIII and XIV; it gave no colour reaction with ferric chloride. Analysis indicated an addition product of equimolar amounts of XIII and methanol. According to its infrared absorption, the methanol adduct contained a non-conjugated and a conjugated carbonyl group (1 720 and 1 670 cm^{-1}). Structure XXI is therefore ascribed to this compound. A colourless solution of XXI in dioxan when acidified with dilute sulphuric acid turned yellow and deposited yellow crystals of XIII. This behaviour is in harmony with the hemiketal structure XXI.

The fact that the melting points of the enol form XIV, the keto form XIII and also of the hemiketal of the latter (XXI) fall within a very narrow range (190—194°) seems to be due to conversion of the enol and the hemiketal into the yellow keto form XIII on heating to temperatures a few degrees below the melting point.

To summarise, the course of the reaction between 2,4-dimethylphenol (I) and periodate, in aqueous solution, can be represented as follows.

Periodate attacks the phenol at the hydroxyl group, producing, possibly by a one-step two-electron transfer¹, the mesomeric aroxyl cation XXII. Addition of water, and loss of a proton, converts XXII competitively into the *p*-quinol II, which is formed in minor amounts, the *o*-quinol III (main



reaction), and the catechol XXIII, the latter being immediately oxidised further to the *o*-quinone XII. While the *p*-quinol (II) is stable, the *o*-quinol III rapidly dimerises by Diels-Alder addition to yield the dimeric *o*-quinol IV, m.p. 237—238°, and simultaneously *o*-quinol III also adds to the *o*-quinone XII with the formation of the *o*-quinol-*o*-quinone adduct XIII, m.p. 193—194°, or its enol form, XIV.

Although *o*-quinones, in dimerisation by a Diels-Alder reaction, act both as diene and as philodiene⁵⁻¹⁰, they were found to act as dienes in adding to another 1,3-diene such as butadiene or *cyclopentadiene*^{22,5}, while the latter behaved as philodienes. The formation of addition product XIII seems to be the first certain case of an *o*-quinone behaving as a philodiene towards a diene component other than a second molecule of the same *o*-quinone. In the present case, the diene component, *i.e.*, the *o*-quinol III, evidently has more pronounced "diene" properties than the *o*-quinone XII, the latter therefore becoming a philodiene in the addition III + XII. Diene activity of *o*-quinol acetates towards typical dienophilic substances as well as towards 1,3-butadiene and *cyclopentadiene* has been demonstrated by Wessely and co-workers^{23,21}. The formation both of the dimeric *o*-quinol (IV) and of the *o*-quinol-*o*-quinone

adduct XIII seems to proceed much more rapidly than the hitherto unknown self-dimerisation of 3,5-dimethyl-*o*-quinone (XII) which also might have been expected to take place in the periodate reaction mixture. Preliminary experiments showed that the latter *o*-quinone is comparatively stable in aqueous solution and will therefore be available for addition to the highly active diene, *o*-quinol III, present in the periodate oxidation mixture.

The primary steps in the oxidation of 2,4-dimethylphenol with periodate as presented in the scheme above are closely analogous to those observed by Wessely and Sinwel²⁴ in the oxidation of the same phenol with lead tetraacetate. The latter reaction yielded the acetate of *o*-quinol III and the diacetate of *o*-quinone XII; the acetate of *p*-quinol II was probably formed also. The differences in the final results of the lead tetraacetate and the periodate reactions, respectively, are due to the greater stability of the monomeric *o*-quinol acetates as compared with the marked tendency of free *o*-quinols to undergo diene addition, as demonstrated in the present paper and in unpublished work¹⁶.

EXPERIMENTAL

Ultraviolet and visible absorption spectra were recorded with a Perkin-Elmer Spectracord 4000-A, infrared spectra with a Perkin-Elmer model 21 instrument (KBr-discs). Analyses by A. Bernhardt, Mülheim (Ruhr), Germany. The determinations of active hydrogen have been carried out by Tekn.lic. R. Magnusson.

Oxidation of 2,4-dimethylphenol with periodate. A stirred solution of 2,4-dimethylphenol (20 g) in water (3.5 l) was mixed with 1.2 l of an aqueous solution of sodium metaperiodate (70 g, molar ratio phenol/periodate = 1/2). After 5 min, ethylene glycol (20 g) was added in order to reduce excess periodate. A light-brown amorphous precipitate (0.8 g) was removed by filtration and the orange-red solution was repeatedly extracted with methylene chloride. The combined extracts were dried over anhydrous calcium sulphate and evaporated leaving a reddish-brown, partly crystalline product.

2,4-Dimethyl-p-benzoquinol (II) (= Substance A). The crude reaction product was treated with ether, in which a minor part of the product dissolved. Concentration of the red ether extract gave a light-red crystalline solid, which was recrystallised several times from benzene-hexane; colourless needles and flat prisms, m. p. 72–73°, identified by infrared absorption (OH, 3 470 cm⁻¹; conjugated CO, 1 670 cm⁻¹) and mixed m. p. with 2,4-dimethyl-*p*-benzoquinol, m. p. 73–73.5°². Yield, about 2%. Recrystallisation from water gave the hydrate, m. p. 53–54°, reported by Bamberger and Bradey².

Dimeric 2,4-dimethyl-o-benzoquinol (IV) (1,2,3,4,4a,7,8,8a-Octahydro-2,8-dihydroxy-2,4a,8,9-tetramethyl-3,7-dioxo-1,4-ethenonaphthalene) (= Substance B). The residue obtained by ether extraction of the crude reaction product was treated with 0.5 N aqueous sodium hydroxide (10 ml per g of the solids). The nearly white insoluble residue was filtered off and washed with water. Recrystallisation from benzene gave colourless prisms, m. p. 237–238°. (Found: C 69.54; H 7.36; active H 0.70; mol. wt. (Rast) 279. Calc. for C₁₆H₂₀O₄: C 69.54; H 7.30; active H 0.72; mol. wt. 276.32). UV spectrum, Fig. 1; IR spectrum, Fig. 2.

Diacetate (IV, OAc instead of OH). a) A mixture of IV (0.58 g), acetic anhydride (7 ml) and anhydrous sodium acetate (0.7 g) was refluxed for 2.5 h. The solvent was removed under reduced pressure and the dark-brown oily residue dissolved in ethanol. Addition of water gave colourless prisms (yield, about 25%), m. p. 183–184° after recrystallisation from ethanol.

b) A 2 M solution of acetic anhydride in ethyl acetate containing 1.15% of perchloric acid²⁵ (12 ml) was added to IV (800 mg), which rapidly dissolved. After 10 min at room temperature, water was added, the ethyl acetate layer repeatedly washed with water and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue recrystallised from ethanol, yielding prisms (76%), identical by m. p. and

mixed m. p. with the product obtained according to a). (Found: C 66.80; H 6.74; CH_3CO 23.04. Calc. for $\text{C}_{20}\text{H}_{24}\text{O}_6$: C 66.65; H 6.71; CH_3CO 23.89.) UV spectrum, Fig. 1.

Treatment of the diacetate with 10 % ethanolic potassium hydroxide for 20 h at room temperature regenerated substance IV, identified by m. p. and mixed m. p. and IR spectrum. Yield, 91 %.

Dihydro derivative of IV (IX) (Decahydro-2,8-dihydroxy-2,4a,8,9-tetramethyl-3,7-dioxo-1,4-ethenonaphthalene). A palladium chloride-barium sulphate catalyst (176 mg), containing 9 % PdCl_2 , was hydrogenated in abs. ethanol (10 ml). A solution of IV (152 mg) in abs. ethanol (30 ml) was added and shaking in a hydrogen atmosphere was continued. After 10 min. 1 mole of H_2 per mole of IV had been consumed and hydrogen uptake ceased. (In 93 % acetic acid instead of ethanol, similar hydrogenation took place but the time required was 30 min.) Evaporation of the filtered ethanol solution gave a colourless crystalline product, needles from ethyl acetate-hexane, m. p. 194–195°. (Found: C 68.73; H 7.85. Calc. for $\text{C}_{16}\text{H}_{22}\text{O}_4$: C 69.04; H 7.97.) IR maxima (cm^{-1}): 3 410 (OH); 1 723 and 1 710 (CO).

Tetrahydro derivative of IV (X) (Decahydro-2,7 (or 3?)-8-trihydroxy-2,4a,8,9-tetramethyl-3 (or 7?)-oxo-1,4-ethenonaphthalene). Platinum oxide (80 mg) was hydrogenated in 93 % aqueous acetic acid (10 ml), and 500 mg IV, dissolved in 10 ml of the same solvent, was added. After 4 min, 1 mole of H_2 , and after a further 150 min, a total of 2 moles of H_2 , had been consumed. Evaporation and recrystallisation from ethyl acetate-hexane gave needles, m. p. 219–220°. (Found: C 68.68; H 8.56. Calc. for $\text{C}_{16}\text{H}_{24}\text{O}_4$: C 68.54; H 8.63.) IR maxima (cm^{-1}): 3 480 and 3 240 (OH), 1 720 (CO), 1 280 (sec. alcohol).

Hexahydro derivative of IV (XI) (Decahydro-2,3,7,8-tetrahydroxy-2,4a,8,9-tetramethyl-1,4-ethenonaphthalene). A solution of IV (1.4 g) in acetic acid (60 ml) was shaken for 24 h, in the presence of 0.17 g PtO_2 , with hydrogen at 3.5 atm. pressure. Evaporation of the filtered solution gave a crystalline residue, which was recrystallised from ethyl acetate-hexane. Prisms, m. p. 201–202°. (Found: C 68.07; H 9.07. Calc. for $\text{C}_{16}\text{H}_{26}\text{O}_4$: C 68.05; H 9.28.) IR maximum at 3 330 cm^{-1} (broad), no carbonyl bands.

Adduct of 2,4-dimethyl-o-quinol and 3,5-dimethyl-o-quinone, enol form (XIV) (1,2,3,4,4a,7 - Hexahydro - 2,8 - dihydroxy - 2,4a,6,9 - tetramethyl - 3,7 - dioxo - 1,4 - ethenonaphthalene) (= Substance C). The orange-yellow alkaline solution obtained after filtering off substance B (see above) was allowed to run fairly rapidly into an excess of glacial acetic acid. The almost white precipitate formed was recovered and recrystallised from glacial acetic acid. Colourless prisms, m. p. 191–192°. (Found: C 69.83; H 6.58; active H 0.92. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_4$: C 70.05; H 6.61; active H 0.73.) IR spectrum, Fig. 3b; UV spectrum, Fig. 4. An alcoholic solution of the substance gave a dark violet-brown colour reaction with alcoholic ferric chloride.

Enol acetate (XV). Acetylation of enol XIV with acetic anhydride in pyridine at room temperature and recrystallisation of the product from ethyl acetate gave the acetate, colourless needles, m. p. 213–214°. No colour reaction with ferric chloride. (Found: C 68.62; H 6.53. Calc. for $\text{C}_{18}\text{H}_{20}\text{O}_5$: C 68.34; H 6.37.) UV spectrum, Fig. 4. IR maxima (cm^{-1}): 3 400 (OH), 1 765 (vinyl ester CO), 1 722 (CO), 1 658 (conj. CO), 1 626 (C=C).

Adduct of 2,4-dimethyl-o-quinol and 3,5-dimethyl-o-quinone, keto form (XIII) (1,2,3,4,4a,7,8,8a-Octahydro-2-hydroxy-2,4a,6,9-tetramethyl-3,7,8-trioxo-1,4 - ethenonaphthalene). A solution of enol XIV (1 g) in 0.5 N aqueous sodium hydroxide (10 ml) was neutralised by dropwise addition of acetic acid. The yellow crystals deposited after cooling were repeatedly recrystallised from ethyl acetate to give yellow prisms, m. p. 194–195°, which gave no colour reaction with alcoholic ferric chloride. (Found: C 70.18; H 6.64; mol. wt. (Rast) 297. Calc. for $\text{C}_{18}\text{H}_{18}\text{O}_4$: C 70.05; H 6.61; mol. wt. 274.30.) UV spectrum, Fig. 4; IR spectrum, Fig. 3a.

Acetylation of XIII with acetic anhydride-pyridine at room temperature gave the enol acetate XV, identical with that obtained from enol XIV. A solution of XIII in acetic anhydride (in the absence of pyridine) was refluxed for 1 h, and the resulting dark-brown solution was poured into water; a dark, amorphous precipitate formed, which was removed by filtration. From the filtrate, unchanged XIII crystallised on cooling.

Quinoxaline derivative from XIII (XX). A solution of XIII (200 mg) and *o*-phenylenediamine (79 mg) in chloroform (50 ml) was kept over anhydrous Na_2SO_4 at room temperature for two weeks. The brown solution was extracted with 0.25 N NaOH , 1 N H_2SO_4 and aqueous NaHCO_3 , and evaporated. The solid residue (190 mg) was recrystallised

from methanol to give slightly yellow prisms, m. p. 161–162°. (Found: C 75.99; H 6.18; N 8.36. Calc. for $C_{22}H_{22}O_2N_2$: C 76.27; H 6.41; N 8.09.)

Methanol addition product of substance XIII (XXI). A hot methanolic solution of the yellow ketone XIII on cooling deposited colourless needles, m. p. 191–192°, which gave no colour reaction with ferric chloride. IR maxima (cm^{-1}): 3 330–3 280 (OH), 1 720 (CO), 1 670 (conj. CO), 1 635 (C=C). (Found: C 66.65; H 7.61; OCH_3 10.20. Calc. for $C_{17}H_{22}O_5$: C 66.65; H 7.24; OCH_3 10.13.)

A sample of XXI was dissolved in cold dioxane. On addition of a drop of dilute aqueous sulphuric acid the colourless solution became yellow, and, on dilution with water, deposited yellow crystals of XIII.

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