Acta Chemica Scandinavica B 28 (1974) 913—921

Diels-Alder Reactions of 2,4-Cyclohexadienones.* IV.** Addition of *o*-Quinols to *p*-Benzoquinones

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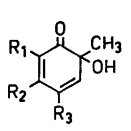
2,6-Dimethylphenol and mesitol were oxidized with aqueous periodate in the presence of an excess of *p*-benzoquinone, toluquinone, 2,6-dimethyl-*p*-benzoquinone or 2,3,5-trimethyl-*p*-benzoquinone. In all cases, the corresponding *o*-quinol-*p*-quinone Diels-Alder adduct was obtained and, in most cases, the *o*-quinol dimer was formed simultaneously. The ratio adduct/dimer was higher with mesitol than with 2,6-dimethylphenol as starting phenol. Furthermore, the yields of adduct increased with decreasing number of methyl substituents in the quinone. No *o*-quinol adducts were obtained with duroquinone.

In each case only one adduct was detected. Spectral and chemical evidence was provided to show that both stereochemical and structural orientation in the adducts were of the same type as previously found in the *o*-quinol dimers.

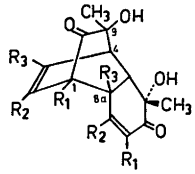
The adducts obtained with *p*-benzoquinone or toluquinone were slowly degraded to 1,4-naphthoquinones by treatment with periodate.

As described earlier,[1-3] periodate oxidation of 2,6-, 2,5-, and 2,4-dimethylphenol, as well as of mesitol, produces the corresponding 6-hydroxy-6-methyl-2,4-cyclohexadienones ("*o*-quinols", *1b – 1e*) which can not be isolated, however, since they undergo rapid self Diels-Alder reaction to give the *o*-quinol dimers *2b – 2e*. Similarly, the parent *o*-quinol *1a*, formed on acid hydrolysis of its acetate, spontaneously dimerizes to compound *2a*.[4]

In all cases, only one dimeric product has been obtained indicating a high degree of both regio- and stereoselectivity of the Diels-Alder dimerizations. All *o*-quinol dimers have the same basic structure involving *endo* configuration and the structural and steric orientation shown in formulae *2a – 2e*.[2,5,6]



1a-f



2a-e

1a, *2a* $R_1=R_2=R_3=H$
1b, *2b* $R_1=CH_3$; $R_2=R_3=H$
1c, *2c* $R_2=CH_3$; $R_1=R_3=H$
1d, *2d* $R_3=CH_3$; $R_1=R_2=H$
1e, *2e* $R_1=R_3=CH_3$; $R_2=H$
1f = *2b*, OAc instead of OH

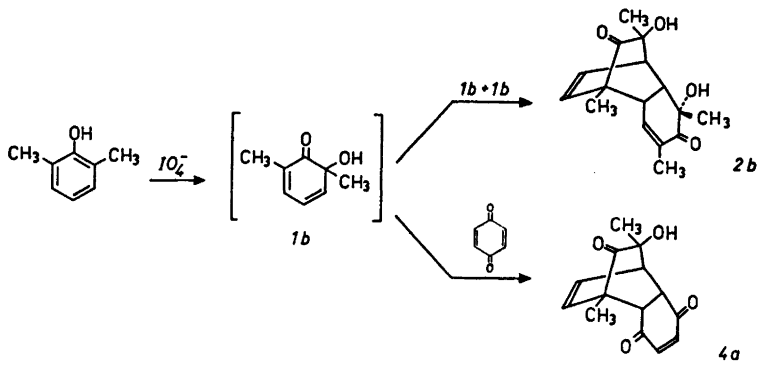
In the present paper we wish to report the trapping of the monomeric *o*-quinols formed on periodate oxidation of 2,6-dimethylphenol and mesitol by *p*-benzoquinones added to the reaction mixture. It was of interest to examine whether the *o*-quinol-*p*-quinone addition reaction involves orientation specificity similar to that encountered in the dimerization of the *o*-quinols.

Formation of *o*-quinol-*p*-quinone adducts

In an attempt to investigate the dienophile character of 2,4-cyclohexadienones, Wessely *et al.*[8] treated an *o*-quinol acetate with typical

* Part XVI in the series "Periodate Oxidation of Phenols". Part XV, see Adler, E., Holmberg, K. and Ryrfors, L.-O. *Acta Chem. Scand. B 28* (1974) 888.

** Part III, see Holmberg, K. *Acta Chem. Scand. B 28* (1974) 857.



Scheme 1.

dienes, *viz.* butadiene and cyclopentadiene. However, in these systems the two last-mentioned compounds added as dienophiles to the *o*-quinol acetate, which acted as diene, indicating a comparatively low dienophile reactivity of the latter compound.

In connection with the present work it may be mentioned that the addition of an *o*-quinol to an *o*-quinone [8] as well as that of another *o*-quinol to a *p*-quinone [9] have been encountered earlier. In both cases the *o*-quinol dimer was formed in addition to the *o*-quinol-quinone adduct. This indicates that the *o*-quinols possessed a dienophile activity comparable to that of the quinones.

In the present work aqueous-ethanolic solutions of 2,6-dimethylphenol or mesitol were added to a solution containing a *p*-benzoquinone (see Table 1) and periodate (molar ratio, 1:1.5:1.1). The competing reactions expected to take place are illustrated in Scheme 1 for the system 2,6-dimethylphenol/*p*-benzoquinone.

The yields of *o*-quinol dimers (*2b*, *2e*) and *o*-quinol-*p*-quinone adducts (*4a*–*h*) formed are listed in Table 1. In each reaction, not more than one product of each type was detected, indicating a high degree of selectivity of both types of Diels-Alder reactions.

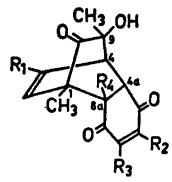
In addition to the dimers and the adducts shown in Table 1, the reactions with 2,6-dimethylphenol gave small amounts of 3,3′,5,5′-tetramethyldiphenoquinone [10] and 2,6-dimethyl-1,4-benzoquinone, whereas those with mesitol yielded minor amounts of 4-hydroxy-2,4,6-trimethyl-2,5-cyclohexadienone (*cf.* also Ref. 1).

The following two conclusions can be drawn from the results presented in Table 1.

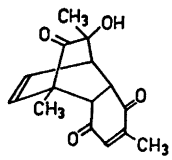
(1) The yield of adduct is higher in the system mesitol/*p*-quinone than in the system 2,6-dimethylphenol/*p*-quinone. This may be understood as follows. Whereas the dienophilic

Table 1. Yields (based on the amount of phenol used) of adducts (*4a*–*4h*) and dimers (*2b*, *2e*) formed on periodate oxidation of 2,6-dimethylphenol and mesitol in the presence of a *p*-benzoquinone.

p-Quinone added	2,6-Dimethylphenol dimer (*2b*)	adduct	Mesitol dimer (*2e*)	adduct
p-Benzoquinone	6	68 (*4a*)	–	78 (*4e*)
Toluquinone	10	73 (*4b*)	–	70 (*4f*)
2,6-Dimethyl-*p*-benzoquinone	66	7 (*4c*)	16	48 (*4g*)
2,3,5-Trimethyl-*p*-benzoquinone	70	2 (*4d*)	18	44 (*4h*)
Duroquinone	40	–	45	–



4a-h, 5



4b'

4a $R_1=R_2=R_3=R_4=H$
4b $R_1=R_2=R_4=H$; $R_3=CH_3$
4c $R_1=R_2=H$; $R_3=R_4=CH_3$
4d $R_1=H$; $R_2=R_3=R_4=CH_3$
4e $R_1=CH_3$; $R_2=R_3=R_4=H$
4f $R_1=R_3=CH_3$; $R_2=R_4=H$
4g $R_1=R_3=R_4=CH_3$; $R_2=H$
4h $R_1=R_2=R_3=R_4=CH_3$
5 = *4a*, OAc instead of OH

double bond, *i.e.* the γ,δ-double bond of the $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl system, is unsubstituted in *o*-quinol *1b*, it possesses a methyl substituent in the γ-position in *o*-quinol *1e*. It is well-known that dienophile reactivity generally decreases with increasing electron density;[7] therefore, due to the electron-releasing effect of the γ-methyl group, *o*-quinol *1e* should be a poorer dienophile than *o*-quinol *1b*. Furthermore, the dimerization of *1e* may be slower than that of *1b* because of steric hindrance exerted by the γ-methyl group present in the former *o*-quinol. Both effects will favour the formation of adducts *4e*–*4h*.

The presence of a γ-methyl substituent has been found to be critical in the dimerization of *o*-quinol acetates. Whereas the *o*-quinol acetates corresponding to *o*-quinols *1a* and *1b* dimerize when heated at 120 °C to give the diacetates of *2a* [4] and *2b*,[1] respectively, the acetates derived from *o*-quinols *1d* and *1e*, possessing a γ-methyl group, proved to be stable even at 160 °C.

(2) The lower the number of methyl substituents in the *p*-benzoquinone, the higher the yield of adduct. This relationship can also be understood to be due to steric and electronic effects, the more heavily methyl substituted *p*-benzoquinone being the poorer dienophile.

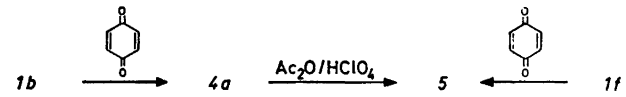
Contrary to the *o*-quinols, their acetates do not undergo Diels-Alder dimerization at room temperature. It was found, however, that a benzene solution of a mixture of *o*-quinol acetate *1f* and *p*-benzoquinone when kept for 10 d at room temperature gave adduct *5* (50 %) as the sole reaction product. Thus *p*-benzoquinone is a better dienophile than the *o*-quinol acetate. Adduct *5* was also obtained by acetylation of the *o*-quinol-*p*-quinone adduct *4a*, indicating analogous structures for the two adducts (Scheme 2).

p-Benzoquinone contains two dienophilic double bonds, and several examples of bis-adducts between *p*-benzoquinone and dienes have been reported.[11] It is known that the formation of the bis-adducts proceeds in two steps, the first diene molecule adding about one hundred times faster than the second one.[11] In the reactions between *p*-benzoquinones and *o*-quinols, however, no bis-adducts have been detected. Furthermore, an attempt to prepare a bis-adduct between *p*-benzoquinone and *o*-quinol *1e* by adding mesitol dropwise to a solution containing a mixture of adduct *4e* and sodium periodate was unsuccessful. The products obtained from the reaction mixture were the *o*-quinol dimer *2e* and unchanged adduct *4e*. Apparently, the adducts of type *4*, for steric reasons, cannot compete as dienophiles with *o*-quinols and *p*-quinones.

The structure of the *o*-quinol-*p*-quinone adducts

The following alternative possibilities regarding the structure of the adducts have to be considered. (*a*) Two structural orientations are conceivable for the adducts *4b*–*4d* and *4f*–*4h*, as exemplified by formulae *4b* and *4b'*. (*b*) The adducts may have *endo* or *exo* configuration. (*c*) The C-9 hydroxyl group may be *anti* and the C-9 methyl group *syn* to the ethylene bridge, or *vice versa*.

The NMR spectra (60 MHz, $CDCl_3$) of the adducts of 2,6-dimethyl- and 2,3,5-trimethyl-



Scheme 2.

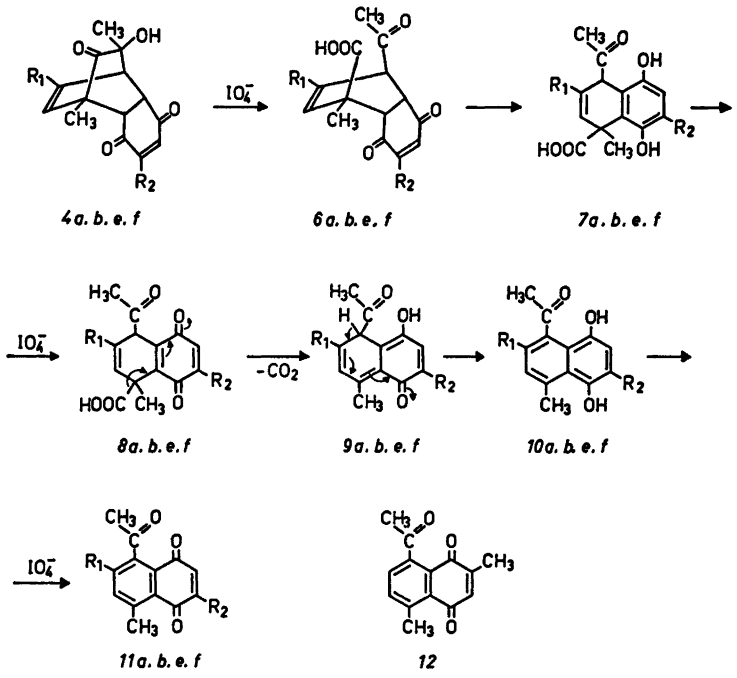
p-benzoquinone clearly showed vicinal coupling between the hydrogen atoms at positions 4 and 4a ($J_{4,4a}=2.0-3.0$ Hz), thus ascertaining the structural orientation of the diene and dienophile moieties to be those shown in the formulae above. In the alternative orientation, represented by formula *4b'*, these adducts would carry a methyl substituent at C-4a.

The structural orientation of the toluquinone adducts could not be clarified by simple NMR analysis. Degradation of the adduct between *o*-quinol *1b* and toluquinone with periodate (see p. 917) gave an acetyl-dimethyl-1,4-naphthoquinone, the m.p. of which (108 – 110 °C) differed from that (150 °C) of a naphthoquinone for which structure *12* has been proposed.[12,13] For this reason, the adduct is assumed to have structure *4b* rather than *4b'*.

By analogy, formula *4f* is assumed for the adduct between toluquinone and *o*-quinol *1e*.

It has been shown that, whereas *o*-quinol dimers *2a – 2c* slowly consume one mol of periodate with cleavage of the 9,10-ketol bridge, dimers *2d* and *2e* are stable towards this oxidant.[6] This has been explained by assuming that the configuration at C-9 is that given in formulae *2*, and that the methyl group at C-8a in dimers *2d* and *2e* prevents the formation of the cyclic periodic ester involving the carbonyl carbon atom at C-10 and the C-9 hydroxyl oxygen atom, which precedes the cleavage reaction. This reasoning, of course, requires *endo* configuration of the dimers.

Periodate oxidation of adducts *4a – 4h* gave the following results. The adducts possessing a methyl group in the 8a-position were stable towards the oxidant, whereas those lacking the angular methyl substituent underwent reaction. The products expected from ketol cleavage, *i.e.* acids *6a*, *6b*, *6e*, and *6f*, however, were



4a. 6a-11a $R_1=R_2=H$
4b. 6b-11b $R_1=H$; $R_2=CH_3$
4e. 6 -11e $R_1=CH_3$; $R_2=H$
4f. 6 -11f $R_1=R_2=CH_3$

Scheme 3.

not obtained from the reactions. Instead, methyl substituted 5-acetyl-1,4-naphthoquinones (*11a*, *11b*, *11e*, and *11f*) were isolated in yields between 52 and 78 % after 2 d reaction time.

A probable pathway for the formation of the naphthoquinones of type *11* is given in Scheme 3. The initial step is believed to be cleavage of the 9,10-ketol bridge of adducts *4* with the formation of carboxylic acids *6*. Aromatization of the enedione ring gives the hydroquinones *7*, which are rapidly oxidized by periodate or iodate to the corresponding *p*-benzoquinones *8*. The latter, being vinylogous β-keto acids, decarboxylate spontaneously to give, via compounds *9*, the 1,4-naphthodiols *10*. These, in turn, are oxidized by periodate or iodate to give the 1,4-naphthoquinones *11*. A similar mechanism has been proposed for the degradation of dimeric *o*-quinones by periodate to give 1,2-naphthoquinones.[14]

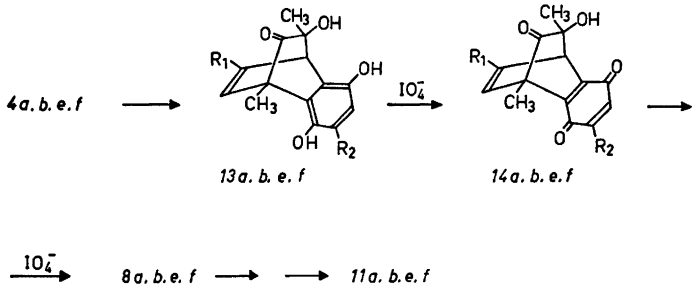
The behaviour of the adducts towards periodate permits the following structural conclusions.

(1) Cleavage of the ketol bridge of the adducts *4a*, *4b*, *4e*, and *4f* by periodate implies that these adducts have *endo* configuration, because an *exo* form of the adducts, similarly to the 8a-methyl substituted *o*-quinol dimers (*2d*, *2e*), would be assumed to be resistant to periodate. By analogy, *endo* configuration is also assigned to the adducts *4c*, *4d*, *4g*, and *4h*, although in these cases experimental evidence is lacking. The exclusive formation of *endo* adducts is in harmony with the behaviour of 2,4-cyclohexadienones in other Diels-Alder reactions.[11]

(2) The resistance to periodate of adducts *4c*, *4d*, *4g*, and *4h*, carrying angular methyl groups at C-8a, indicates that the C-9 hydroxyl group in these adducts is oriented *anti* to the ethylene bridge (compare the analogous behaviour of C-8a substituted *o*-quinol dimers.[6] See also p. 916). This high degree of selectivity regarding the steric orientation at C-9, earlier recognized in the dimerization of *o*-quinols,[6] can be ascribed to steric approach control,[11] the bulky methyl group being directed away from the reaction center. It then seems justified to assume the same steric arrangement at C-9 for adducts *4a*, *4b*, *4e*, and *4f*.

It might be argued that, instead of following pathway *A* presented in Scheme 3, the conversion *4*→*11* may proceed by the alternative route *B* shown in Scheme 4. The initial step of route *B* would be aromatization of the enedione ring of the adducts *4a*, *4b*, *4e*, and *4f* to give the hydroquinones *13*. Rapid oxidation to the *p*-quinones *14*, followed by periodate cleavage of the ketol bridge, would lead to the *p*-quinones *8*, which would be converted into naphthoquinones *11* by the mechanism given in Scheme 3.

If the conversion *4*→*11* proceeds by route *B*, it would not be possible to draw any conclusions regarding *endo* or *exo* configuration of the adducts, since both forms would give rise



Scheme 4.

to the same intermediate hydroquinones *13*.

The following observations, however, speak against pathway *B*.

Firstly, the acetate *5* of adduct *4a* would be expected to be stable towards periodate if ketol cleavage is the primary step (route *A*), but would be transformed into the acetate of *p*-benzoquinone *14a* (*via* the 9-acetyl derivative of hydroquinone *13a*) if *B* is the proper route. Route *A* was supported by the finding that acetate *5* remained unchanged on 2 d treatment with periodate.

Secondly, whereas adduct *4a*, similar to the behaviour of other enediones,[15,16] is smoothly converted into the hydroquinone *13a* by alkali, acid-induced aromatization, which would be involved in the primary step of mechanism *B* (Scheme 4), proceeds less readily. Adduct *4a* proved to be stable in glacial acetic acid and was only slowly transformed into hydroquinone *13a* by 10 % aqueous-ethanolic sulphuric acid, *13a* being obtained in a yield of only 20 % after two days treatment. It is not probable, therefore, that adducts *4* on treatment with aqueous-ethanolic $NaIO_4$ (pH 4 – 5), in a first reaction step, would undergo the aromatization to *13* shown in Scheme 4.

The isolated hydroquinone *13a*, when treated with excess periodate gave the naphthoquinone *11a*. Using a 1:1 ratio of *13a* and periodate, the *p*-benzoquinone *14a* could be isolated, and further oxidation of the latter compound produced the naphthoquinone *11a*. These results support the mechanism for the conversion *13a*→*11a* given in Scheme 4.

It is known that the ethylenic bond of the enedione system of *p*-benzoquinone adducts is easily hydrogenated with zinc/acetic acid.[16,17] The dihydroadduct *15*, obtained in this way from adduct *4a*, on treatment with periodate gave the carboxylic acid *16* (see Scheme 5). This finding lends further support to the assignment of *endo* configuration to adduct *4a*, since the *exo* form of *15* should presumably be resistant towards the oxidizing agent.

There is, however, a possibility for *15* to undergo *exo-endo* interconversion via the dienol. Such an isomerization by base has been reported for a similar adduct.[18] Considering the behaviour of the adducts of type *4* in the presence of acid (see above), however, it seems improbable that isomerization of *15* would take place in acetic acid or aqueous periodate solutions.

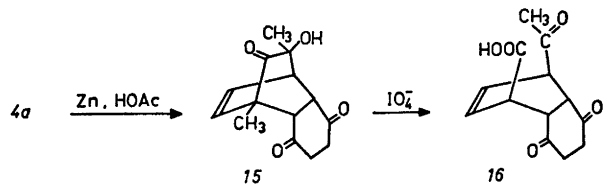
The NMR spectra of adducts *4a* – *4h* were in agreement with the assigned structures. As an example, the NMR signals given by *4a* are reported on p. 919. Similarly, the NMR spectra of the 1,4-naphthoquinones of type *11* have been exemplified by the spectrum of *11a* (p. 920), the spectra of the remaining naphthoquinones also being in accord with the proposed structures.

The UV spectra of the adducts

The β,γ-enone system present in the adducts *4a* – *4h* is expected to give rise to a transannular charge transfer band around 210 nm.[6,19,20] However, such bands were visible above 200 nm only in the spectra of the adducts *4e* – *4h*, obtained from *o*-quinol *1e*.

The three further absorption bands can be ascribed to the enedione system.[16,21] The band around 290 nm (column 2) is enhanced by the overlapping $n\rightarrow\pi^*$ absorption of the β,γ-unsaturated carbonyl system.[1] Although the Woodward rules cannot be applied properly to enediones,[22] the position of the $\pi\rightarrow\pi^*$ bands (column 1) are within the expected range, increasing methyl substitution causing increasing batochromic shift.[15]

The position of the bands listed in columns 2 and 3 are in harmony with data given in the literature for similar enediones.[16,21] Both bands show a hypsochromic shift with increasing methyl substitution of the ethylenic bond. This



Scheme 5.

Table 2. UV maxima in nm and log ε values (in parentheses) of *o*-quinol-*p*-quinone adducts *4a – 4h*. Solvent: ethanol.

Adduct	β,γ-Enone	Enedione 1	2	3
4a		217 (4.08)	290 (2.64)	378 (2.05)
4b		235 (4.11)	284 (2.73) sh	375 (2.07)
4c		236 (3.96)	284 (2.60) sh	375 (2.02)
4d		249 (4.03)	272 (3.42) sh	365 (2.11)
4e	203 (4.70)	222 (4.44) sh	305 (2.77)	383 (2.12)
4f	206 (4.51)	236 (4.22) sh	292 (2.78)	375 (2.16)
4g	213 (4.10) sh	235 (4.11)	288 (2.70) sh	374 (2.07)
4h	213 (4.05)	245 (4.06)	280 (3.20) sh	370 (2.06)

effect becomes clear also from the colours of the adducts, which change from bright yellow (*4a* and *4e*) via light yellow (*4b*, *4c*, *4f*, and *4g*) to almost colourless (*4d* and *4h*).

The transannular charge transfer bands of compounds *4e – 4h* are overlapped to some degree by the adjacent $\pi \rightarrow \pi^*$ bands of the enedione system, which affects their ε values. In the dihydroadduct *15*, where only the former band is present (λ_{max} 204 nm), the log ε value is 3.63, in agreement with values for similar compounds.[19]

EXPERIMENTAL

UV spectra were recorded on a Cary Model 14 spectrophotometer; IR and NMR spectra were obtained using Beckman 9A and Varian A-60 instruments, respectively. Chemical shifts are given in δ (ppm units with TMS used as internal standard).

o-Quinol-p-quinone adducts 4a – 4h. A solution of the phenol (2,6-dimethylphenol or mesitol, 0.010 mol) in ethanol-water 1:1 (20 ml) was added dropwise during a 10 min period to a solution of a mixture of sodium metaperiodate (0.011 mol) and the *p*-benzoquinone (*p*-benzoquinone, toluquinone, 2,6-dimethyl-*p*-benzoquinone, or 2,3,5-trimethyl-*p*-benzoquinone, 0.015 mol) in ethanol-water 1:2 (180 ml). After further 15 min excess periodate was destroyed by 4 ml of ethylene glycol. Red crystals of 3,3′,5,5′-tetramethyldiphenoquinone were filtered off from the oxidation mixtures of 2,6-dimethylphenol. Yield, 1 %; m.p. after recrystallization from chloroform 203 – 210 °C (lit.[19] 207 – 217 °C).

The solution was then extracted with three 40 ml portions of hexane, which removed the major part of the *p*-quinone, and subsequently with dichloromethane, and the latter extract was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a silica gel column using benzene-ethyl acetate (4:1). The R_F values of the *o*-quinol-*p*-quinone adducts were between 0.14 and 0.18 and those of the *o*-quinol dimers between 0.08 and 0.11. The products were recrystallized from ethanol. Yields, see Table 1. *o*-Quinol dimers *2b* and *2e* were shown to be identical by mixed m.p. with authentic samples.[1]

1,4,4a,8a-Tetrahydro-9-hydroxy-1,9-dimethyl-1,4-ethanonaphthalene-5,8,10-trione (4a). M.p. 162 – 163 °C. (Found: C 68.53; H 5.66. Calc. for $C_{14}H_{14}O_4$: C 68.28; H 5.73). UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1612 (C=C), 1675 (conj. CO), 1730 (CO), 3410 (OH). NMR (DMSO-d_6): δ 1.08 and 1.17 (singlets, 3 H each, 2 CH_3), 2.95 (d, 1 H, H-8a), 3.28 (ddd, 1 H, H-4), 3.67 (dd, 1 H, H-4a), 5.81 (dd, 1 H, H-2), 5.91 (s, 1 H, OH), 6.37 (dd, 1 H, H-3), 6.79 (s, 2 H, H-6 and H-7). $J_{2,3}=8$ Hz, $J_{2,4}=2$ Hz, $J_{3,4}=6$ Hz, $J_{4,4a}=3$ Hz, $J_{4a,8a}=9$ Hz.

1,4,4a,8a-Tetrahydro-9-hydroxy-1,7,9-trimethyl-1,4-ethanonaphthalene-5,8,10-trione (4b). M.p. 171.5 – 172.5 °C. (Found: C 69.23; H 6.20. Calc. for $C_{15}H_{16}O_4$: C 69.21; H 6.20). UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1625 (C=C), 1665 (conj. CO), 1715 (CO), 3420 (OH).

1,4,4a,8a-Tetrahydro-9-hydroxy-1,7,8a,9-tetramethyl-1,4-ethanonaphthalene-5,8,10-trione (4c). M.p. 146 – 147 °C. (Found: C 70.0; H 6.7. Calc. for $C_{16}H_{18}O_4$: C 70.1; H 6.6). UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1620 (C=C), 1655 (conj. CO) 1730 (CO), 3400 (OH).

1,4,4a,8a-Tetrahydro-9-hydroxy-1,6,7,8a,9-pentamethyl-1,4-ethanonaphthalene-5,8,10-trione (4d). M.p. 148 – 149 °C. (Found: C 70.7; H 7.1. Calc. for $C_{17}H_{20}O_4$: C 70.8; H 7.0). UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1630 (C=C), 1660 (conj. CO), 1720 (CO), 3410 (OH).

1,4,4a,8a-Tetrahydro-9-hydroxy-1,3,9-trimethyl-1,4-ethanonaphthalene-5,8,10-trione (4e). M.p. 110 – 111 °C. (Found: C 69.02; H 6.30. Calc. for $C_{15}H_{16}O_4$: C 69.21; H 6.20.) UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1610 (C=C), 1665 (conj. CO), 1720 (CO), 3410 (OH).

1,4,4a,8a-Tetrahydro-9-hydroxy-1,3,7,9-tetra-

methyl-1,4-ethanonaphthalene-5,8,10-trione (4f). M.p. 165–166 °C. (Found: C 70.02; H 6.59. Calc. for $C_{16}H_{18}O_4$: C 70.05; H 6.61). UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1625 (C=C), 1670 (conj. CO), 1725 (CO), 3380 (OH).

1,4,4a,8a-Tetrahydro-9-hydroxy-1,3,7,8a,9-pentamethyl-1,4-ethanonaphthalene-5,8,10-trione (4g). M.p. 170–171 °C (Found: C 70.70; H 7.01. Calc. for $C_{17}H_{20}O_4$: C 70.81; H 6.99). UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1635 (C=C), 1660 (conj. CO), 1715 (CO), 3430 (OH).

1,4,4a,8a-Tetrahydro-9-hydroxy-1,3,6,7,8a,9-hexamethyl-1,4-ethanonaphthalene-5,8,10-trione (4h). M.p. 164–165 °C. (Found: C 71.08; H 7.26. Calc. for $C_{18}H_{22}O_4$: C 71.50; H 7.33). UV, see Table 2. IR (KBr): ν_{max}, cm^{-1} 1630 (C=C), 1670 (conj. CO), 1720 (CO), 3410 (OH).

Oxidation of 2,6-dimethylphenol and mesitol with periodate in the presence of duroquinone: A solution of the phenol (5.0 mmol) in ethanol-water 1:1 (10 ml) was added dropwise during a period of 10 min to a solution of sodium metaperiodate (5.5 mmol) and duroquinone (7.5 mmol) in ethanol-water 3:2 (225 ml). After an additional 15 min, ethylene glycol (2 ml) was added to reduce excess periodate. The reaction mixture was worked up as described above. Thin layer chromatography indicated that no adducts had been formed. The crude reaction products on treatment with acetone/hexane gave the *o*-quinol dimers *2b* and *2e*, respectively, identified by mixed m.p. with authentic samples.[1] Yields, see Table 1.

Acetate 5. (*a*) *By acetylation of adduct* 4a. The adduct was treated with the $Ac_2O/HClO_4$ reagent according to Ref. 23. M.p. 147–149 °C after recrystallization from ethanol. Yield, 72 %. (Found: C 66.3; H 5.5. Calc. for $C_{16}H_{16}O_5$: C 66.66; H 5.60). IR (KBr): ν_{max}, cm^{-1} 1612 (C=C), 1680 (conj. CO), 1740 (CO and ester CO). The NMR spectrum ($CDCl_3$) shows a singlet at δ 2.10 (3 H) due to the ester $-CH_3$.

(*b*) *From* o-*quinol acetate* 1f *and* p-*benzoquinone.* *p*-Benzoquinone (2.0 g) and *o*-quinol acetate *1f*[24] (2.0 g) were dissolved in 20 ml of dry benzene. The mixture was kept for 10 d in the dark at room temperature. The solvent was then removed and the residue treated with 40 ml of ether. The crystals deposited were recrystallized from ethanol. A 50 % yield of acetate *5* was obtained, identical with the product obtained according to (*a*) by mixed m.p. and spectroscopic data.

Naphthoquinones 11a, 11b, 11e, *and* 11f. A solution of 2.5 g of sodium metaperiodate in 100 ml of water was added to a solution of 1.0 g of the adduct (*4a*, *4b*, *4e*, or *4f*) in 750 ml of ethanol-water 1:2. After 2 d at room temperature the solution was extracted with dichloromethane. The extract was dried over anhydrous Na_2SO_4 and brought to dryness under vacuum. The residue, on treatment with ether, gave yellow crystals, which were recrystallized from ethanol.

5-Acetyl-8-methyl-1,4-naphthoquinone (11a). Yield, 78 %. M.p. 142–144 °C. (Found: C 72.59; H 4.73. Calc. for $C_{13}H_{10}O_3$: C 72.89; H 4.71). UV (ethanol): λ_{max}, nm (log ε) 240 (4.31), sh 323 (3.30), 351 (3.42). IR (KBr): ν_{max}, cm^{-1} 1550, 1585 and 1610 (arom. ring and C=C), 1660 and 1705 (CO). NMR ($CDCl_3$): δ 2.48 (s, 3 H, CH_3-8), 2.78 (s, 3 H, CH_3CO), 6.93 (s, 2 H, H-2 and H-3), 7.33 and 7.59 (doublets, 1 H each, H-6 and H-7, $J_{6,7}=8$ Hz).

5-Acetyl-2,8-dimethyl-1,4-naphthoquinone (11b). Yield, 68 %. M.p. 108–110 °C. (Found: C 73.78; H 5.31. Calc. for $C_{14}H_{12}O_3$: C 73.67; H 5.30). UV (ethanol): λ_{max}, nm (log ε) 248 (4.24), 353 (3.42). IR (KBr): ν_{max}, cm^{-1} 1550, 1590 and 1630 (arom. ring and C=C), 1660, 1695 and 1710 (CO).

5-Acetyl-6,8-dimethyl-1,4-naphthoquinone (11e). Yield, 63 %. M.p. 113–114 °C. (Found: C 73.7; H 5.3. Calc. for $C_{14}H_{12}O_3$: C 73.67; H 5.30). UV (ethanol): λ_{max}, nm (log ε) 250 (4.26), 356 (3.46). IR (KBr): ν_{max}, cm^{-1} 1542, 1586 and 1614 (arom. ring and C=C), 1660 and 1702 (CO).

5-Acetyl-2,6,8-trimethyl-1,4-naphthoquinone (11f). Yield, 52 %. M.p. 156–157 °C. (Found: C 74.2; H 5.8. Calc. for $C_{15}H_{14}O_3$: C 74.36; H 5.83). UV (ethanol): λ_{max}, nm (log ε) 253 (4.27), 358 (3.48). IR (KBr): ν_{max}, cm^{-1} 1549, 1591 and 1630 (arom. ring and C=C), 1658 and 1700 (CO).

1,4-Dihydro-5,8,9-trihydroxy-1,9-dimethyl-1,4-ethanonaphthalen-10-one (13a). (*a*) *By alkaline treatment of* 4a. A solution of 2.5 g of adduct *4a* in 150 ml of ethanol was added dropwise, in a nitrogen atmosphere, to ice-cold 1.25 M aqueous NaOH (125 ml). Twenty min after the addition had been completed, the mixture was neutralized with dil. HCl and then extracted with chloroform. The extract was dried over anhydrous Na_2SO_4 and evaporated. Recrystallization of the residue from ethanol gave a 76 % yield of *13a*, m.p. 290–292 °C. (Found: C 68.18; H 5.72. Calc. for $C_{14}H_{14}O_4$: C 68.28; H 5.73). UV (ethanol): λ_{max}, nm (log ε) sh 210 (4.18), sh 235 (3.79), 308 (3.59). IR (KBr): ν_{max}, cm^{-1} 1492, 1600, 1620 (arom. ring), 1708 (CO), 3250 and 3370 (OH). NMR (DMSO-d_6): δ 1.28 (s, 3 H, CH_3-9), 1.73 (s, 3 H, CH_3-1), 4.29 (dd, 1 H, H-4), 5.09 (s, 1 H, OH-9), 6.10 (dd, 1 H, H-2), 6.46 (s, 2 H, H-6 and H-7), 6.61 (dd, 1 H, H-3), 8.60 (s, 2 H, OH-5 and OH-8). $J_{2,3}=7.5$ Hz, $J_{2,4}=2$ Hz, $J_{3,4}=6.5$ Hz.

(*b*) *By acid treatment of* 4a. A solution of adduct *4a* (0.5 g) in 10 % ethanolic sulphuric acid (150 ml) was kept for 2 d at room temperature, then diluted with water and extracted with chloroform. Evaporation of the extract gave *13a* in a 20 % yield, identical with the product obtained according to (*a*) by mixed m.p. and spectroscopic data.

1,4-Dihydro-9-hydroxy-1,9-dimethyl-1,4-ethanonaphthalene-5,8,10-trione (14a). A solution of sodium metaperiodate (0.85 g, 4 mmol) in water (100 ml) was added to hydroquinone

13a (0.98 g, 4 mmol) in ethanol-water 2:5 (700 ml). After 5 min, excess periodate was removed by addition of 5 ml ethylene glycol, and the solution was extracted with chloroform. Removal of the solvent from the combined extracts gave a crystalline residue. Recrystallization from ethanol gave *14a*, m.p. 166–168 °C, in a 64 % yield. (Found: C 68.71; H 4.90. Calc. for $C_{14}H_{12}O_4$: C 68.84; H 4.95). UV (ethanol): λ_{max}, nm (log ε) sh 210 (4.13), 247 (4.19), sh 310 (2.97), 352 (2.95). IR (KBr): ν_{max}, cm^{-1} 1577 and 1605 (C=C), 1655 (conj. CO), 1722 (CO), 3460 (OH). NMR ($CDCl_3$): δ 1.43 (s, 3 H, CH_3-9), 1.85 (s, 3 H, CH_3-1), 2.85 (s, 1 H, OH), 4.53 (dd, 1 H, H-4), 6.14 (dd, 1 H, H-2), 6.52 (t, 1 H, H-3), 6.66 (s, 2 H, H-6 and H-7). $J_{2,3}=J_{3,4}=7$ Hz, $J_{2,4}=2$ Hz.

Naphthoquinone 11a. (*a*) *From* 13a. A solution of 2.0 g of sodium metaperiodate in 100 ml of water was added to 0.50 g of hydroquinone *13a* dissolved in 300 ml ethanol-water 1:2. After 24 h the solution was extracted with chloroform. Evaporation of the extract gave yellow crystals of *11a*, m.p. after recrystallization from ethanol 142–144 °C. Identical by mixed m.p. with the product obtained from periodate oxidation of adduct *4a*.

(*b*) *From* 14a. A mixture of 2.0 g of sodium metaperiodate and 0.50 g of *14a* dissolved in 400 ml of ethanol-water 1:2 was kept at room temperature for 24 h. Extraction with chloroform gave crystals of *11a*, m.p. after recrystallization from ethanol 142–144 °C. Identical by mixed m.p. with the product obtained according to (*a*).

1,4,4a,6,7,8a-Hexahydro-9-hydroxy-1,9-dimethyl-1,4-ethanonaphthalene-5,8,10-trione (15). Zinc powder (2.0 g) was added in portions to a stirred solution of 1.0 g of adduct *4a* in 40 ml acetic acid-water 2:1. After 20 min, the mixture was filtered and the filtrate concentrated to a volume of 10 ml. Water was added and the solution extracted with dichloromethane. The extract was dried over anhydrous Na_2SO_4 and evaporated, yielding almost colourless crystals. Recrystallization from benzene/hexane gave *15*, m.p. 109–110 °C, in a 66 % yield. (Found: C 67.75; H 6.50. Calc. for $C_{14}H_{16}O_4$: C 67.73; H 6.53). UV (ethanol): λ_{max}, nm (log ε) sh 204 (3.63), 306 (2.22). IR (KBr): ν_{max}, cm^{-1} 1655 (C=C), 1697 and 1720 (CO), 3390 (OH).

4-Acetyl-1,4,4a,6,7,8a-hexahydro-1-methyl-5,8-dioxo-1-naphthalenecarboxylic acid (16). A solution of sodium metaperiodate (1.0 g) in 75 ml water was added to a solution of dihydroadduct *15* (0.50 g) in 75 ml ethanol-water 2:3. After 16 h the solution was extracted with chloroform. The extract was dried over anhydrous Na_2SO_4 and concentrated to a volume of 10 ml. The crystals deposited were recrystallized from ethanol to give *16*, m.p. 167–168 °C, in a 80 % yield. (Found: C 63.9; H 6.1. Calc. for $C_{14}H_{16}O_5$: C 63.62; H 6.10). UV (ethanol): λ_{max}, nm (log ε) 283 (2.36). IR (KBr): ν_{max}, cm^{-1} 1710 (CO), 2300–3300 (COOH). The NMR spectrum (DMSO-d_6) shows a singlet at δ 2.22 (3 H) due to the CH_3CO group.

Acknowledgements. The authors are greatly indebted to Professor E. Adler for his kind interest and valuable advice.

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Received March 8, 1974.