Reactions of 4-Hydroxycyclohexa-2,5-dienones under Acidic Conditions

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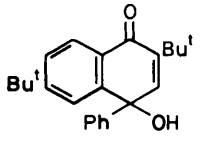
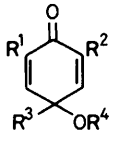
The 4-hydroxy-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone (2) undergoes reaction in acidic conditions to give, *inter alia*, derivatives of an arene-1,2-diol. In poorly nucleophilic media, the 1,1'-biphenyl-4-ol (16) and the 5-phenyl-*o*-benzoquinone (37) are the main products. Isolation of the 4-(2-methylpropyl)cyclohexadienone derivatives (41) and (42) provides the first examples of intermolecular trapping of a four-carbon unit. The products are consistent with the intervention of the phenoxenium ion (44); the formation of the 2-methyl-1,3-benzodioxole (43) testifies to the intermediacy of such a powerful oxidant. Whereas the 4-phenyl-2-t-butyl-*p*-quinol (5) gave a complex mixture from which only the 1,1'-biphenyl-4-ol derivative (24) was isolated, the 2,6-di-isopropyl- and 2,6-dimethyl-analogues (4) and (6) afforded mainly the arene-1,3-diol derivatives (48) and (47), respectively. The 4-methyl-2,6-di-t-butyl-*p*-quinol (7) gave products [*e.g.* (28) and (29)] arising from nucleophilic attack on an intermediate *p*-quinone methide; dimers were the major products in the absence of a good nucleophile.

TREATMENT of 4-substituted 4-hydroxycyclohexa-2,5-dienones (*p*-quinols) with acid usually affords derivatives of a *meta*- or *para*-arenediol *via* a dienone–phenol type of rearrangement.[1,2] However, we reported recently[3] that the major rearranged products from treatment of the *p*-quinols (1), (2), and (3) with Ac_2O–H_2SO_4 at room temperature were the *ortho*-arenediol diacetates (11), (12), and (13), respectively. Moore and Kirk[4] also have



(1)



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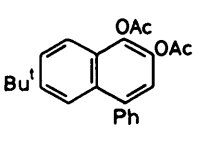
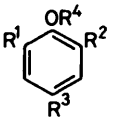


(11)

(2) $R^1 = R^2 = Bu^t$, $R^3 = Ph$, $R^4 = H$
(3) $R^1 = R^2 = Bu^t$, $R^3 = p\text{-}MeOC_6H_4$, $R^4 = H$
(4) $R^1 = R^2 = Pr^i$, $R^3 = Ph$, $R^4 = H$
(5) $R^1 = R^4 = H$, $R^2 = Bu^t$, $R^3 = Ph$
(6) $R^1 = R^2 = Me$, $R^3 = Ph$, $R^4 = H$
(7) $R^1 = R^2 = Bu^t$, $R^3 = Me$, $R^4 = H$
(8) $R^1 = R^2 = Bu^t$, $R^3 = Ph$, $R^4 = Me$
(9) $R^1 = R^2 = Bu^t$, $R^3 = Ph$, $R^4 = Ac$
(10) $R^1 = R^2 = R^4 = H$, $R^3 = Me$

recorded the isolation of the pyrocatechol derivative (12) from the reaction of the 2,6-di-t-butyl-*p*-quinol (2) with Ac_2O or with Ac_2O–H_2SO_4, and of the halogenophenols (14) and (15), using concentrated HCl or HBr–HOAc, respectively. We now report the results of the reactions of the sterically congested cyclohexadienone (2) in a variety of acidic media, together with the results of analogous reactions of the 2,6-di-isopropyl-4-phenyl-*p*-quinol (4), the 4-phenyl-2-t-butyl-*p*-quinol (5), the 2,6-dimethyl-4-phenyl-*p*-quinol (6), and the 4-methyl-2,6-di-t-butyl-*p*-quinol (7).

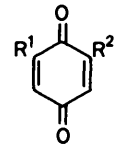
The substrates (2)—(5) were synthesized[5] by the reaction of a substituted *p*-benzoquinone with the appropriate Grignard reagent.[6] Conversion of 2,6-di-isopropyl-*p*-benzoquinone (33) into the 4-hydroxy-4-phenylcyclohexadienone (4) was improved by the inclusion of hexamethylphosphoric triamide (1 mol equiv.) in the reaction medium.[7] While this general approach has the merits of being direct and experimentally simple, the required adducts were isolated in moderate yields only (30—60%), and reproducibility was often a problem;[8] this was probably due to conjugate addition and/or electron-transfer processes competing with the desired 1,2-arylation or alkylation at the less hindered carbonyl group.



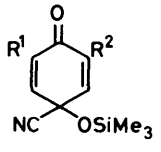
(12) $R^1 = Bu^t$, $R^2 = OAc$, $R^3 = Ph$, $R^4 = Ac$
(13) $R^1 = Bu^t$, $R^2 = OAc$, $R^3 = p\text{-}MeOC_6H_4$, $R^4 = Ac$
(14) $R^1 = Bu^t$, $R^2 = Cl$, $R^3 = Ph$, $R^4 = H$
(15) $R^1 = Bu^t$, $R^2 = Br$, $R^3 = Ph$, $R^4 = H$
(16) $R^1 = R^2 = Bu^t$, $R^3 = Ph$, $R^4 = H$
(17) $R^1 = Bu^t$, $R^2 = OAc$, $R^3 = Ph$, $R^4 = H$
(18) $R^1 = Bu^t$, $R^2 = OH$, $R^3 = Ph$, $R^4 = Ac$
(19) $R^1 = Bu^t$, $R^2 = SAc$, $R^3 = Ph$, $R^4 = Ac$
(20) $R^1 = Bu^t$, $R^2 = OMe$, $R^3 = Ph$, $R^4 = H$
(21) $R^1 = R^2 = Bu^t$, $R^3 = p\text{-}MeOC_6H_4$, $R^4 = Ac$
(22) $R^1 = Bu^t$, $R^2 = OH$, $R^3 = Ph$, $R^4 = H$
(23) $R^1 = R^2 = Bu^t$, $R^3 = p\text{-}MeOC_6H_4$, $R^4 = H$
(24) $R^1 = Bu^t$, $R^2 = H$, $R^3 = Ph$, $R^4 = Ac$
(25) $R^1 = Bu^t$, $R^2 = H$, $R^3 = Ph$, $R^4 = H$
(26) $R^1 = R^2 = Me$, $R^3 = Ph$, $R^4 = Ac$
(27) $R^1 = R^2 = Pr^i$, $R^3 = Ph$, $R^4 = Ac$
(28) $R^1 = R^2 = Bu^t$, $R^3 = CH_2OH$, $R^4 = Ac$
(20) $R^1 = R^2 = Bu^t$, $R^3 = CH_2OAc$, $R^4 = Ac$
(30) $R^1 = R^2 = Bu^t$, $R^3 = CH_2OAc$, $R^4 = H$
(31) $R^1 = R^2 = Bu^t$, $R^3 = CH_2OH$, $R^3 = H$

A sequence which potentially overcomes the problem of formation of regioisomeric 1,2-adducts has been introduced by Evans.[9,10] Thus, reaction of 2,6-dimethyl-*p*-benzoquinone (32) with cyanotrimethylsilane, catalyzed by potassium cyanide–18-crown-6 in anhydrous carbon tetrachloride under reflux, results in cyanosilylation at the most electrophilic carbon atom to afford the 3,5-dimethylcyclohexadienone (36). However, steric effects may become dominant in appropriate cases. For example, 2,6-di-t-butyl-*p*-benzoquinone gave the regioisomer (34),[9] while in the present work the 2,6-di-isopropyl analogue (33) gave only the dienone (35), after extended reaction times, and 2,6-di-t-butyl-1,4-naphthoquinone failed to react at all, even in tetrachloroethylene under reflux. Treatment of the protected 2,6-dimethylcyclohexadienone (36) with phenylmagnesium bromide, followed by regeneration of the carbonyl group with

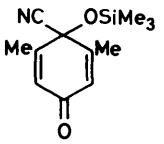
silver(I) fluoride in aqueous tetrahydrofuran (THF), gave the required *p*-quinol (6) in an acceptable overall yield (47%).



(32) $R^1 = R^2 = Me$
(33) $R^1 = R^2 = Pr^i$



(34) $R^1 = R^2 = Bu^t$
(35) $R^1 = R^2 = Pr^i$



(36)

4-Hydroxy-4-methyl-2,6-di-t-butylcyclohexa-2,5-dienone (7) was synthesized in 97% yield *via* the base-catalyzed oxygenation of 4-methyl-2,6-di-t-butylphenol.[11]

The products isolated from treatment of the *p*-quinol (2) with acid under a variety of conditions are recorded in the Table. In Ac_2O–H_2SO_4 the *ortho*-diacetate (12) [3,4] intermediate was deduced from the results of a reaction of the *p*-quinol (2) conducted at room temperature in Ac_2S–H_2SO_4 [13] (entry 6, Table). One of the products was 4-acetylthio-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone (40) (14%). The *ortho*-disubstituted aromatic compound analogous to the biphenyl (12), *viz* the monoacetylthio-derivative (19), was the major product when either sulphuric acid (entry 6) or BF_3·Et_2O (entry 8) was used as a catalyst. This product may arise from the intramolecular delivery of an acetylthio-moiety from C-4 of the dienone (40), or more probably *via* the external nucleophilic attack of sulphur on a carbocationic intermediate. Similarly, use of MeOH–$HClO_4$ (entry 9) gave the 4-methoxycyclohexadienone (8) as the major product; [4] the methoxybiphenyl (20) was also isolated in low yield, together with the biphenyl-4-ol (16) and the *o*-benzoquinone (37).

With the intermediacy of the acetate (9) established and the structure of the major *ortho*-diacetate product

Products [a] from treatment of the *p*-quinol (2) with acid

Reagent	Temp. (0 °C)	Time (h)	(2)	(8)	(9)	(12)	(16)	(17)	(18)	(19)	(20)	(37)	(38)	(30)	(40)	(41)	(42)	(43)
Ac_2O–H_2SO_4	20	1				44	4	10	5			4	6	4		8		
Ac_2O–H_2SO_4	20	24				57								9			3	
Ac_2O–H_2SO_4	−78 [c]	0.08 [b]	55 [d]		45 [d]													
Ac_2O–H_2SO_4	−78 [c]	1 [b]			50 [d]	50 [d]												
Ac_2O–H_2SO_4	−78 [c]	1 [c]						60 [d]	40 [d]									
Ac_2S–H_2SO_4	20	24					18			23					14			
Et_2O–BF_3·Et_2O	20	7					26										18	20
Ac_2S–BF_3·Et_2O	20	24					10			60								
MeOH–$HClO_4$	20	24		49			13				8	5						
Et_2O–$HClO_4$	20	24	15				33					29						
CH_2Cl_2–CF_3SO_3H	20	1					45					32						
$MeNO_2$–CF_3SO_3H	20	1					42					28						

[a] Isolated (p.l.c.) yields. [b] Ac_2O–H_2SO_4 was transferred by syringe into a solution of compound (2) in Ac_2O at −78 °C. [c] Ac_2O–H_2SO_4 was placed inside a sealed glass bulb which was placed in the substrate solution. Both solutions were cooled to −78 °C and the sealed bulb was then broken to allow mixing to occur. [d] ^1H N.m.r. analysis. [e] Quenched at −78 °C by addition of Et_3N.

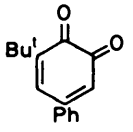
was the major product after either 1 or 24 h at room temperature.* These conditions are milder than those used by Moore and Kirk [4] who reported that this reaction was sluggish, requiring several days at 100—110 °C. On the contrary, a series of experiments which we carried out at −78 °C showed not only that the reaction proceeds significantly at this temperature within 1 h (entries 4 and 5, Table 4), but also that an intermediate *p*-quinol acetate (9) could be detected (entries 3 and 4, Table). An authentic sample of this acetate was synthesized in high yield by the reaction of the *p*-quinol (2) with acetic anhydride–triethylamine–4-(*N*,*N*-dimethylamino)pyridine; these conditions effected the esterification of the tertiary hydroxy-group more rapidly (18 h) than the use of acetic anhydride–pyridine (6 d). The acetate (9) was shown to undergo acid-catalyzed rearrangement at room temperature to give a product distribution identical with that obtained from similar treatment of the *p*-quinol (2). The fact that the *p*-quinol acetate (9) arises from the external attack of a carboxylate anion on a carbocationic

* The cleanest route to the diacetate (12) (99%) involved the reaction of the *p*-quinol (2) with Ac_2O–NaOAc.[12]

(12) secure,[3] it was of interest to isolate and identify the minor products present after a compatatively short reaction time at room temperature (entry 1). 3,5-Di-t-butyl-1,1′-biphenyl-4-ol (16) was recovered in the same yield (4%) as 5-phenyl-3-t-butyl-*o*-benzoquinone [3] (37), suggesting that the formation of this pair of products occurs *via* a mutual redox process.[4] The structures of the dimers (38) and (39) were supported by elemental composition data, and by their spectra. The conversion of the hydroxy-acetate (38) into the diacetate (39) as the reaction proceeds is indicated by the relative yields of these dimers after 1 and 24 h. The isomeric monomeric hydroxy-acetates (17) and (18) were each present after 1 h, and both of these compounds are converted into the diacetate (12).

The remaining compound isolated from the 1-h reaction (entry 1) was assigned the structure 4-(2-acetoxy-2-methylpropyl)-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone (41). An accurate mass measurement on the molecular ion at *m/z* 396 confirmed the molecular formula as $C_{26}H_{36}O_3$. The mass spectrum also contained significant peaks, corresponding to the loss of acetic acid

and of (C_4H_8 + HOAc) from the molecular ion, which indicate that the acetate group is bound to an alkyl carbon atom. The i.r. spectrum contained absorptions due to an alkyl acetate group (1 735 cm^{-1}) and an αβ-unsaturated carbonyl group (1 660 and 1 630 cm^{-1}), while a maximum at 246 nm in the u.v. spectrum confirmed the presence of a cross-conjugated dienone. In the ^1H n.m.r. spectrum the signal due to the t-butyl protons occurred as a singlet at δ 1.25, that due to the vinyl protons as a singlet at δ 6.67, and that due to the



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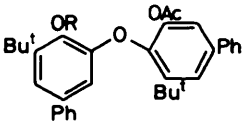
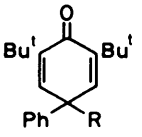


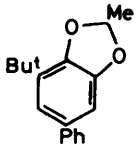
(38) R = H
(39) R = Ac



(40) R = SAc
(41) R = $CH_2C(OAc)Me_2$
(42) R = $CH_2C(Me)=CH_2$

phenyl protons as a broadened singlet at δ 7.22. The attachment of a 2-acetoxy-2-methylpropyl moiety at C-4 of a cyclohexa-2,5-dienone was suggested by the singlet due to an isolated methylene group at δ 2.73, by the singlet at δ 1.40 due to a *gem*-dimethyl group subtended on an oxygen-bearing carbon atom, and by the singlet due to the aliphatic acetate methyl protons at δ 1.92. A related compound, 4-(2-methylprop-2-enyl)-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone (42) was isolated in low yield from the reaction in Ac_2O–H_2SO_4 for 24 h (entry 2), and in higher yield when $BF_3{\cdot}Et_2O$ was used as the catalyst (entry 7). When the latter experiment was carried out in the presence of added t-butyl alcohol the yield of compound (42) increased from 18 to 39%. That compound (42) was a 4-phenylcyclohexa-2,5-dienone was confirmed by its spectral data, and the nature of the other substituent at C-4 was deduced as follows. Consideration of the molecular formula ($C_{24}H_{32}O$) required the substituent to be a C_4H_7 unit, while signals in the ^1H n.m.r. spectrum at δ 1.60, 2.78, 4.55, and 4.73 were characteristic of a 2-methylprop-2-enyl group; each of these signals showed the expected broadening due to allylic coupling. Although de-t-butylation is an established feature of reactions occurring in acidic media *via* cationic intermediates,[14-16] and is shown in the present work by the formation of compounds (12), (17), (18), (37), (38), and (39) in Ac_2O–H_2SO_4, to our knowledge compounds (41) and (42) represent the first examples where an ejected four-carbon unit has been trapped intermolecularly to generate a 4,4-disubstituted dienone.

In addition to the 4-(2-methylprop-2-enyl)cyclohexadienone (42), the *ortho*-diol derivative 2-methyl-6-phenyl-4-t-butyl-1,3-benzodioxole (43) was isolated consistently, albeit unexpectedly, from treatment of the *p*-quinol (2) with $BF_3{\cdot}Et_2O$ in diethyl ether; the molecular formula ($C_{18}H_{20}O_2$) was established by microanalysis. In the mass spectrum the base peak (*m/z* 253) arises *via* the facile expulsion of a methyl radical from the molecular ion (*m/z* 268). The ^1H n.m.r. spectrum confirmed the presence of only one t-butyl group. A doublet (*J* 5 Hz) and a quartet (*J* 5 Hz) at δ 1.67 and 6.15 accord with the data reported [17] for the resonance positions of the 2-methyl group and heterocyclic methine proton, respectively, in the parent 2-methyl-1,3-benzodioxole. In the SFORD ^{13}C n.m.r. spectrum, the monoprotonated carbon atom of the heterocyclic ring gave rise to a doublet at relatively low field (δ 105.4) as expected; the attached methyl group occurred at δ 20.8. In order to prove unequivocally that structure (43) was correct, this compound was synthesized by an alternative route. Although the most obvious procedure involves condensation of 5-t-butyl-1,1′-biphenyl-3,4-diol (22) with acetaldehyde, in practice [17] this method requires extended reaction times and the use of a large excess of aldehyde, and then affords only a moderate yield. A number of procedures [18] involving the use of a dihalogenomethane in a dipolar aprotic solvent, or under phase-transfer catalysis, are effective for the synthesis of 1,3-benzodioxole itself, but application of a similar approach to the synthesis of the 2-methyl homologue (43) suffers from



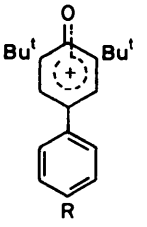
(43)

competitive elimination processes from the required 1,1-dihalogenoethane. In the present work, the dioxole (43) was produced by treatment of the pyrocatechol (22) with vinyl acetate in the presence of $BF_3{\cdot}Et_2O$ and HgO; [19] the product was identical with that isolated from the *p*-quinol (2). In order to determine that the ethylidene unit in compound (43) was derived from diethyl ether, and not, for example, *via* a four carbon moiety arising from a t-butyl carbocation (*cf.* ref. 20), the *p*-quinol (2) was treated with $BF_3{\cdot}Et_2O$ in [$^2H_{10}$]diethyl ether. From this medium the tetradeuterioisotopomer, 2-[$^2H_3$]methyl-6-phenyl-4-t-butyl-[2-$^2H_1$]-1,3-benzodioxole, was isolated, together with the undeuteriated analogue (43), in the ratio 62 : 38.

The 1,1′-biphenyl-4-ol (16) was the major product from reaction of *p*-quinol (2) in $BF_3{\cdot}Et_2O$–Et_2O. When either $HClO_4$ (entry 10, Table) or CF_3SO_3H (entries 11 and 12) were used as the catalyst in non-nucleophilic solvents this biphenylol and the related [4] *o*-benzoquinone (37) were the only products, and were isolated in comparable yields.

As expected for a process involving intervention of a carbocationic intermediate, the 4'-methoxyphenyl *p*-quinol (3) reacted in Ac_2O–H_2SO_4 more rapidly than the parent compound (2), and gave the arene-1,2-diol diacetate (13) (62%),[3] and the 1,1'-biphenylyl acetate (21) (5%).

The formation of the products from these acid-catalyzed reactions can be rationalized by invoking the intermediacy of a phenoxenium ion, *e.g.* (44) (red-violet

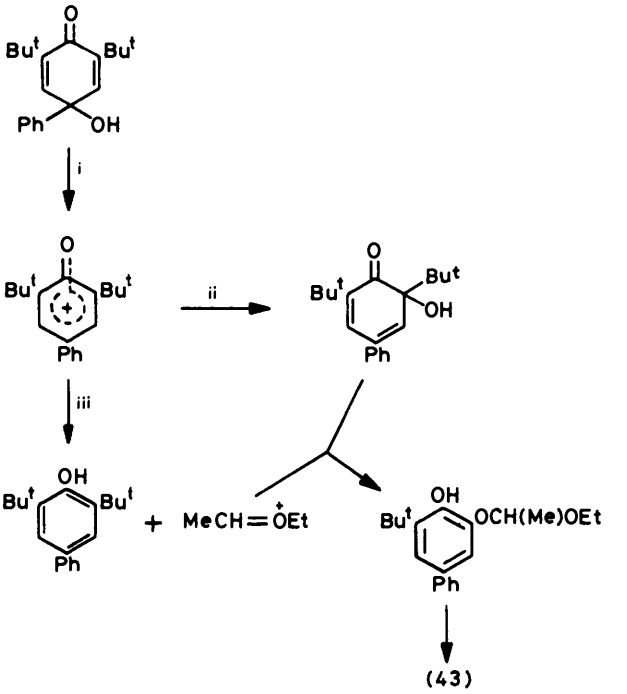


(44) R = H
(45) R = OMe
(46) R = NMe_2

colour), arising *via* attack of an electrophile (usually a proton) at the tertiary alcohol group of a *p*-quinol, followed by heterolysis. The ion (45) has been generated and characterized by two-electron anodic oxidation of the biphenylol (23), while the 4'-*N*,*N*-dimethylamino-species (46) forms an isolable salt with poorly nucleophilic counter-ions.[21] Although the parent ion (44) has not been isolated, its intervention as a product-forming intermediate in the reactions reported here is established. Nucleophilic attack at C-3 of the ion (44), followed by de-t-butylation and concomitant aromatisation, leads to the arene-1,2-diol derivatives. Moreover, the ion (44) will be a powerful oxidant; the analogue (45) has been shown [21] to regenerate the biphenylol (23) on addition of water and therefore is easily reducible. Thus, attack on the phenoxenium ion (44) by water on quenching provides a route to biphenylol (16). However, there is evidently some correspondence (entries 9—12) between the yields of compound (16) and of the related *o*-benzoquinone (37), suggesting that this pair may be generated *in situ*, and that their formation is coupled.[4]

Protonation at the tertiary hydroxy-group in the *p*-quinols (2) and (3) contrasts with the behaviour of the uncongested 4-methyl-*p*-quinol (10) for which it has been established [22] that protonation (in $HClO_4$–H_2O) occurs at the carbonyl oxygen atom, leading eventually to the *para*-product, 2-methylbenzene-1,4-diol.

Formation of the 1,3-benzodioxole (43) from the reaction of compound (1) in BF_3·Et_2O–Et_2O merits further comment. No reaction occurred when benzene-1,2-diol was treated with acetaldehyde and BF_3·Et_2O in diethyl ether at room temperature for 48 h, which suggests that the reactive species involved in the formation of compound (43) are not the pyrocatechol (22) and acetaldehyde itself. There is, however, a literature precedent for the formation of an oxonium ion precursor of acetaldehyde ($R\dot{O}$=$CHCH_3$) in the reaction of diethyl ether with an Ar_3CCl–$AlCl_3$ reagent,[23] and a general scheme for the production of oxonium ions in the presence of Lewis acids (including BF_3·Et_2O) has been given by Perst.[24] Moreover, an example involving transfer of hydride from an ethoxy-group to a carbocation to generate $R\dot{O}$=$CHCH_3$ has been reported recently.[25] In the present case (see Scheme) the phenoxenium ion is available as a potent hydride acceptor; interception of the resulting alkyloxonium ion by the 6-hydroxycyclohexa-2,4-dienone leads to the 1,3-benzodioxole (43).



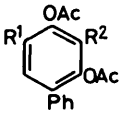
SCHEME *Reagents*: i, BF_3·Et_2O; ii, $^-BF_3OH$; iii, Et_2O

Treatment of 4-hydroxy-4-phenyl-2-t-butylcyclohexa-2,5-dienone (5) with Ac_2O–H_2SO_4 at room temperature for 3.5 h gave a mixture containing at least ten compounds. The only component recovered in a pure state was 3-t-butyl-1,1'-biphenyl-4-yl acetate (24) (19%). The use of milder reaction conditions (2.8×10^{-3} mol l^{-1} of H_2SO_4 in Ac_2O, 0 °C, 30 min) did not simplify the product mixture; only the biphenylol (25) (20%) was isolated in a pure state.

In contrast to the 4-hydroxy-2,6-di-t-butylcyclohexa-2,5-dienones (2) and (3), the 2,6-dimethyl analogue (6) underwent reaction in Ac_2O–H_2SO_4 to give mainly the expected [1,2] product of a dienone–phenol rearrangement, *viz* the 1,3-diacetate (47). This diacetate was deduced to be the *meta*- rather than the *para*-isomer on the basis of ^{13}C n.m.r. substituent chemical-shift additivity parameters.[26] With this substrate, therefore, product formation is initiated primarily by protonation of the carbonyl oxygen atom (see above). The biphenyl-4-yl acetate (40) (15%) was the only other product.

The *p*-quinol (4), in which isopropyl groups flank the carbonyl oxygen atom, was synthesized to provide a sub-

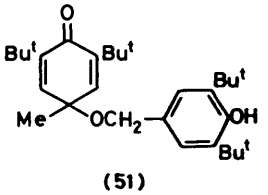
strate with a potential carbocationic leaving group whose stability is intermediate between the extremes represented by the t-butyl group in (2) and the methyl group in (6). In the event, treatment of compound (4) with Ac_2O–H_2SO_4 gave the 1,3-diacetate (48) as the rearrangement product, together with the biphenyl-4-yl acetate



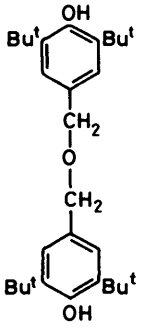
(47) $R^1 = R^2 = Me$
(48) $R^1 = R^2 = Pr^i$
(49) $R^1 = Pr^i$, $R^2 = C(OAc)Me_2$
(50) $R^1 = Me$, $R^2 = CH_2OAc$

(27) (7 : 3). A detailed examination of the ^1H n.m.r. spectra of the crude products from the reaction of the *p*-quinols (4) and (6) in Ac_2O–H_2SO_4 indicated the presence also of the benzylic acetates (49) [δ 2.00, s, $Me_2C(OAc)$] and (50) (δ 4.98, s, CH_2OAc), respectively. The formation of these products, albeit in trace amounts, indicates the operation of a minor reaction pathway initiated by protonation of the hydroxy-group, followed by loss of water and deprotonation, to generate an *o*-quinone methide. 1,4-Addition of acetate anion leads to the benzylic acetates. The phenoxenium ion (44) cannot undergo deprotonation to a quinone methide.

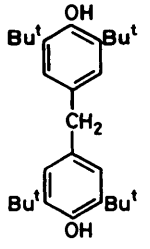
The intermediacy of isomeric *p*-quinone methides [27] was evident from the structures of the products isolated from the reaction of the 4-methyl-2,6-di-t-butyl-*p*-quinol (7) with acid. Thus, both the benzylic alcohol (28) and its acetate (29) (*cf.* ref. 28) were formed in Ac_2O–H_2SO_4. Although treatment of the acetate (29) with methanolic potassium carbonate readily afforded the alcohol (28), it was shown to be stable to the work-up and isolation conditions used in the acid-catalyzed reaction; acetylation of compound (28) occurred easily under these conditions. In HOAc–H_2SO_4 the isomeric monoacetate [29] (30) was the major product, as expected. The formation of the benzylic alcohol (28) in Ac_2O–H_2SO_4 therefore implicates the hydrogensulphate anion as an alternative nucleophile, sulphur-oxygen fission occurring during work-up or isolation. When the solvent was not a good nucleophile source, dimers were the major products. Thus, $BF_3{\cdot}Et_2O$–Et_2O afforded the unsymmetrical dimer (51) as the only product *via* 1,6-addition of the *p*-quinol (7) to a *p*-quinone methide. Both compound (51) and the symmetrical dimer (52) were isolated from THF–$HClO_4$, together with a low yield of the monomeric benzyl alcohol (31). When the pure cyclohexa-2,5-dienone (51) was treated with THF–$HClO_4$, both the dimer (52) and alcohol (31) were detected (t.l.c.), indicating that conversion of compound (51) into the dimer (52) occurs *via* the reaction of the alcohol (31) with a *p*-quinone methide. A separate experiment showed that both dimers were formed also from the alcohol (31). Treatment of the 4-methyl-*p*-quinol (7) with the perfluorosulphonic acid resin Nafion-H [30] in 1,2-dimethoxyethane gave compounds (31), (51), (52), and also the methylene-bridged symmetrical dimer (53) [31] in low yield. Formation of the last-named product requires the loss of one carbon atom and is suggested to occur *via ipso*-protonation of the alcohol (31) at C-1 to generate the carbocation (54). Expulsion of formaldehyde and a proton affords 2,6-di-t-butylphenol, leading to the dimer (53) by reaction either with the alcohol (31) or with the derived *p*-quinone methide.



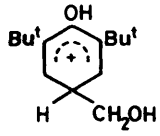
(51)



(52)



(53)



(54)

EXPERIMENTAL

General experimental details are reported in ref. 3.

Preparation of 4-Hydroxy-2,6-dimethyl-4-phenylcyclohexa-2,5-dienone (6).—Cyanotrimethylsilane (1.25 ml, 9.9 mmol) was added to a solution of 2,6-dimethyl-*p*-benzoquinone [32] (0.95 g, 7.0 mmol) and freshly prepared potassium cyanide–18-crown-6 complex [from KCN (5 mg) and 18-crown-6 (19 mg) in anhydrous MeOH (2 ml)] in dry carbon tetrachloride (6 ml). The solution was heated under reflux for 10 h and then kept at room temperature overnight. The solvents were removed under reduced pressure from the crude 4-cyano-3,5-dimethyl-4-trimethylsiloxycyclohexa-2,5-dienone [9] (36), and diethyl ether (2 ml) was introduced. This solution was added to phenylmagnesium bromide (from bromobenzene; 7.5 mmol) in dry diethyl ether (18 ml) at −78 °C. After 4 h the reaction was quenched by the addition of saturated aqueous ammonium chloride and worked up to give a brown syrup (2.17 g). This material was dissolved in tetrahydrofuran (THF) (20 ml), a solution of silver(I) fluoride (0.93 g, 7.4 mmol) in water (5 ml) was added, and the mixture was stirred at room temperature overnight. Work-up followed by p.l.c. (hexane–diethyl ether, 7 : 3) gave *4-hydroxy-2,6-dimethyl-4-phenylcyclohexa-2,5-dienone* (6) (702 mg, 47%) as colourless prisms, m.p. 92.5—93 °C (from CCl_4) (Found: C, 78.8; H, 6.8. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%), $\lambda_{max.}$ 230 nm (log ε 4.15); $\nu_{max.}$ 3 610 (free OH), 3 425 (bonded OH), 1 665 and 1 640 cm^{-1} (conjugated CO); δ_H 1.87 (s, Me), 2.80 (s, exchangeable on deuteriation, OH), 6.58 (s, 3-H and 5-H), and 7.11—7.57 (m, ArH); *m/z* 214 ($M^{+\cdot}$), 199, and 196; δ_C 15.8 (Me), 71.0

(C-4), 125.2 (C-3′ and C-5′), 127.9 (C-4′), 128.7 (C-2′) and C-6′), 133.0 (C-2 and C-6), 140.3 (C-1′), 146.7 (C-3 and C-5), and 187.3 p.p.m. (C-1).

Preparation of 4-*Hydroxy*-2,6-*di-isopropyl*-4-*phenylcyclohexa*-2,5-*dienone* (4).—A solution of phenylmagnesium bromide (from bromobenzene, 7.6 mmol) in dry diethyl ether (10 ml) was added during 10 min to a solution of 2,6-di-isopropyl-*p*-benzoquinone (477 mg, 2.5 mmol) in dry diethyl ether (15 ml) at −78 °C. After 2 h at this temperature, the reaction was quenched by the addition of saturated aqueous ammonium chloride. Work-up, followed by p.l.c. (hexane–diethyl ether, 2 : 1), gave (in order of decreasing R_F): (i) 4-*hydroxy*-2,6-*di-isopropyl*-4-*phenylcyclohexa*-2,5-*dienone* (4) (280 mg, 42%), b.p. (Kugelrohr) 130 °C at 0.1 mmHg (Found: C, 80.2; H, 8.5. $C_{18}H_{22}O_2$ requires C, 79.95; H, 8.2%), $\lambda_{max.}$ 226 nm (log ε 4.28); $\nu_{max.}$ 3 600 (free OH), 3 460 (bonded OH), 1 668, and 1 640 cm^{-1} (conjugated CO); δ_H 1.07 (d, *J* 7 Hz, CH*Me*$_2$), 2.28br (s, exchangeable on deuteriation, OH), 3.02 (sp. *J* 7 Hz, C*H*Me$_2$), 6.47 (s, 3-H and 5-H), and 7.08—7.47 (m, ArH); *m/z* 270.1612 ($M^{+\bullet}$; $C_{18}H_{22}O_2$ requires 270.1619), 228, 213, 185, and 105; and (ii) 4-*hydroxy*-3,5-*di-isopropyl*-4-*phenylcyclohexa*-2,5-*dienone* (29 mg, 4%), as colourless needles, m.p. 181—182 °C (from hexane–diethyl ether) (Found: C, 80.0; H, 8.4. $C_{18}H_{22}O_2$ requires C, 79.95; H, 8.2%), $\lambda_{max.}$ 273 (log ε 3.51) and 227 nm (4.31); $\nu_{max.}$ 3 420 (OH), 1 668, and 1 622 cm^{-1} (conjugated CO); δ_H 0.60 [d, *J* 7 Hz, CH(*Me*)Me], 1.22 [d, *J* 7 Hz, CH(Me)*Me*], 2.50 (sp, *J* 7 Hz, C*H*Me$_2$), 3.75br (s, exchangeable on deuteriation, OH), 5.92 (s, 2-H and 6-H), and 7.00—7.18 (m, ArH); *m/z* 270.1609 ($M^{+\bullet}$; $C_{18}H_{22}O_2$ requires 270.1619), 228, 213, and 185.

Repetition of this experiment with the inclusion of hexamethylphosphoric triamide (1 equiv.) gave the *p*-quinol (4) (52%).

Attempted synthesis of the *p*-quinol (4) *via* the cyanosilylation–Grignard sequence (see above) was unsuccessful because the cyanosilylation step (room temperature, 8 d) produced only 4-cyano-2,6-di-isopropyl-4-trimethylsiloxycyclohexa-2,5-dienone (35), $\nu_{max.}$ 2 325 (C≡N), 1 655 (conjugated CO), and 1 612 cm^{-1} (conjugated C=C); δ_H 1.10 [d, *J* 7 Hz, CH(*Me*)Me], 1.15 [d, *J* 7 Hz, CH(Me)*Me*], 3.02 (sp, *J* 7 Hz, C*H*Me$_2$), and 6.43 (s, 3-H and 5-H); δ_C 21.1 [CH(*Me*)Me], 21.3 [CH(Me)*Me*], 26.6 (*C*HMe$_2$), 64.8 (C-4), 117.6 (CN), 134.8 (C-3 and C-5), 146.1 (C-2 and C-6), and 182.8 p.p.m. (C-1).

Preparation of 4-*Hydroxy*-4-*phenyl*-2-*t-butylcyclohexa*-2,5-*dienone* (5).—A solution of phenylmagnesium bromide (from bromobenzene, 12.8 mmol) in dry diethyl ether (60 ml) was added dropwise to a solution of 2-t-butyl-*p*-benzoquinone (1.51 g, 9.3 mmol) in dry diethyl ether (50 ml) at −78 °C. The deep-blue mixture was stirred at this temperature for 2 h and quenched with saturated aqueous ammonium chloride. Work-up, followed by p.l.c. (hexane–diethyl ether, 4 : 1), gave: (i) starting material (809 mg); and (ii) 4-hydroxy-4-phenyl-2-t-butylcyclohexa-2,5-dienone (5) (420 mg, 41% based on starting material) as an unstable oil (Found: $M^{+\bullet}$, 242.1319. $C_{16}H_{18}O_2$ requires $M^{+\bullet}$, 242.1306), $\lambda_{max.}$ 223 nm (log ε 3.73); $\nu_{max.}$ 1 680 and 1 640 cm^{-1} (conjugated CO); δ_H 1.18 (s, C*Me*$_3$), 3.50br (s, exchangeable on deuteriation, OH), 5.93 (d, *J* 9 Hz, 6-H), 6.58 (s, 3-H), 6.62 (d, *J* 9 Hz, 5-H), and 7.00—7.47 (m, ArH); *m/z* 242, 227, 199, and 186.

Acid-catalyzed Reactions of 4-*Hydroxy*-4-*phenyl*-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (2).—(a) *In* Ac_2O–H_2SO_4. Concentrated sulphuric acid (3 drops) was added to a solution of the *p*-quinol (2) (0.60 g, 2.0 mmol) in acetic anhydride (3 ml). The red-violet solution was kept at room temperature for 1 h and then poured onto ice. Work-up, followed by p.l.c. (hexane–diethyl ether, 3 : 1) gave: (i) 3,5-di-t-butyl-1,1′-biphenyl-4-ol (16) (24 mg, 4%) as colourless needles, m.p. 100—102 °C (from pentane–diethyl ether) (lit.,[4] 101—103 °C) (Found: C, 85.2; H, 9.4. Calc. for $C_{20}H_{26}O$: C, 85.1; H, 9.3%), $\lambda_{max.}$ 260 nm (log ε 4.55); $\nu_{max.}$ 3 648 and 1 240 cm^{-1} (OH); δ_H 1.50 (s, C*Me*$_3$), 5.03 (s, exchangeable on deuteriation, OH), and 7.07—7.42 (m, ArH); *m/z* 282 ($M^{+\bullet}$), 267, and 57; δ_C 30.4 (C*Me*$_3$), 34.5 (*C*Me$_3$), 124.0 (C-2 and C-6), 126.4 (C-4′), 127.0 (C-2′ and C-6′), 128.6 (C-3′ and C-5′), 132.6 (C-1), 136.1 (C-3 and C-5), 143.0 (C.1′), and 153.5 p.p.m. (C-4); (ii) 3-(3-acetoxy-5-t-butyl-1,1′-biphenyl-4-oxy)-5-t-butyl-1,1′-biphenyl-4-ol (38) (32 mg, 6%) (Found: $M^{+\bullet}$, 508.2627. $C_{34}H_{36}O_4$ requires $M^{+\bullet}$, 508.2614), $\lambda_{max.}$ 254 nm (log ε 4.43); $\nu_{max.}$ 3 425 (OH), 1 725, and 1 222 cm^{-1} (OAc); δ_H 1.48 (s, CMe$_3$), 1.52 (s, CMe$_3$), 1.93br (s, exchangeable on deuteriation, OH), 2.43 (s, OAc), 6.70 (d, *J* 2 Hz, 2-H and 2′-H or 6-H and 6′-H), and 7.07—7.58 (m, ArH); *m/z* 508, 466, 282, 267, 226, 57, and 43; (iii) 4-(2-*acetoxy*-2-*methylpropyl*)-4-*phenyl*-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (41) (63 mg, 8%), b.p. 142—143 °C at 0.01 mmHg (Found: C, 78.6; H, 9.0. $C_{26}H_{36}O_3$ requires C, 78.8; H, 9.1%), $\lambda_{max.}$ 246 nm (log ε 3.78); $\nu_{max.}$ 1 735 (AcO), 1 660, and 1 630 cm^{-1} (conjugated CO); δ_H 1.25 (s, CMe$_3$), 1.40 (s, Me), 1.92 (s, OAc), 2.73 (s, CH$_2$), 6.67 (s, 3-H and 5-H), and 7.22 (s, ArH); *m/z* 396.2670 ($M^{+\bullet}$; $C_{26}H_{36}O_3$ requires 396.2664), 336, 298, and 280; (iv) 3-(3′-*acetoxy*-5-*t-butyl*-1,1′-*biphenyl*-4-*oxy*)-5-*t-butyl*-1,1′-*biphenyl*-4-*yl acetate* (39) (21 mg, 4%) as white prisms, m.p. 207—209 °C (from pentane–diethyl ether) (Found: C, 78.2; H, 7.2. $C_{36}H_{38}O_5$ requires C, 78.5; H, 7.0%), $\lambda_{max.}$ 245 nm (log ε 4.43); $\nu_{max.}$ 1 770 and 1 210 cm^{-1} (AcO); δ_H 1.43 [s, C(Me)$_3$], 2.30 (s, OAc), 7.00 (d, *J* 2 Hz, 2-H and 2′-H or 6-H and 6′-H), and 7.07—7.53 (m, ArH); *m/z* 550 ($M^{+\bullet}$, <1%), 508, 226, 211, and 57; δ_C 21.0 (OCO*Me*), 30.3 (C*Me*$_3$), 35.0 (*C*Me$_3$), 115.6 (C-2 and C-2″), 120.7 (C-6 and C-6″), 127.1 (C-2′, C-2‴, C-6′, and C-6‴), 127.3 (C-4′ and C-4‴), 128.6 (C-3′, C-3‴, C-5′, and C-5‴), 139.0 (C-1 and C-1″), 140.2 and 140.5 (C-1′, C-1‴, C-4, and C-4″), 143.4 (C-5 and C-5″), 148.9 (C-3 and C-3″), and 168.8 p.p.m. (*O*COMe); (v) 5-t-butyl-1,1′-biphenyl-3,4-diyl diacetate [3] (12) (284 mg, 44%) m.p. 116.5—118.5 °C; (vi) 5-phenyl-3-t-butyl-*o*-benzoquinone [3] (37) (19 mg, 4%) as dark-red prisms, m.p. 121—122 °C; and (vii) a mixture (2 : 1) (86 mg) of 4-hydroxy-5-t-butyl-1,1′-biphenyl-3-yl acetate (17) (10%) and 3-hydroxy-5-t-butyl-1,1′-biphenyl-4-yl acetate (18) (5%), m.p. 130—132 °C [lit.,[4] 134—136 °C for (17)] [Found: C, 76.0; H, 7.0. Calc. for $C_{18}H_{20}O_3$ (mixture): C, 76.0; H, 7.1%], $\lambda_{max.}$ 314 (log ε 3.81) and 249 nm (4.10); $\nu_{max.}$ 3 580 and 3 420 (OH), 1 775 and 1 745 cm^{-1} (aromatic OAc); δ_H 1.35 [s, CMe$_3$ of (18)], 1.45 [s, CMe$_3$ of (17)], 2.30 [s, OAc of (17)], 2.35 [s, OAc of (18)], 6.75 [d, *J* 2 Hz, 6-H of (18)], 6.83 [d, *J* 2 Hz, 2-H of (18)], and 7.10—7.63 (m, ArH); *m/z* 284 ($M^{+\bullet}$), 242, and 227.

When the reaction was allowed to continue for 24 h 4-(2-*methylprop*-2-*enyl*)-4-*phenyl*-2,6-*di-t-butyl*-*cyclohexa*-2,5-*dienone* (42) (20 mg, 3%) was also obtained as an oil (Found: C, 85.9; H, 9.3. $C_{24}H_{32}O$ requires C, 85.7; H, 9.5%), $\lambda_{max.}$ 235 nm (log ε 4.0); $\nu_{max.}$ 1 652 and 1 640 cm^{-1} (conjugated CO); δ_H 1.23 (s, CMe$_3$), 1.60 (s, Me), 2.78 (s, CH$_2$), 4.55 (m, =CH$_2$), 6.50 (s, 3-H and 5-H), and 7.15 (s, ArH); *m/z* 336.2426 ($M^{+\bullet}$; $C_{24}H_{32}O$ requires 336.2451), 280, 265, and 223; δ_C 24.4 (Me), 29.3 (C*Me*$_3$), 34.8 (*C*Me$_3$), 46.9 (C-4), 47.4 (CH$_2$), 115.4 (=CH$_2$), 126.1 (C-3′ and C-5′), 126.9 (C-4′), 128.7 (C-2′ and C-6′), 140.9 (C-2 and C-6),

142.5 (C-1'), 145.4 (C-3, C-5, and C=CH_2), and 186.2 p.p.m. (C-1).

From reactions carried out at −78 °C, 4-acetoxy-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone [14] (9) was a major product. It was identical (^{1}H n.m.r.) with an authentic sample synthesized by treating the *p*-quinol (2) with acetic anhydride in triethylamine containing a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine.

(b) *In* Ac_2S–H_2SO_4. Concentrated sulphuric acid (3 drops) was added to a solution of the *p*-quinol (2) (110 mg, 0.37 mmol) in acetic thioanhydride (1.5 ml). The red-violet solution was kept at room temperature for 24 h and then poured into water. Work-up, followed by p.l.c. (hexane–diethyl ether, 3 : 1) gave: (i) the 1,1'-biphenyl-4-ol (16) (12 mg, 18%); (ii) 4-acetylthio-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone (40) (19 mg, 14%) as an oil, δ_H 1.27 (s, CMe_3), 2.23 (s, SCO*Me*), 6.77 (s, 3-H and 5-H), and 7.10—7.50 (m, ArH); and (iii) 5-*acetylthio*-3-*t*-*butyl*-1,1'-*biphenyl*-4-*yl acetate* (19) (29 mg, 23%), m.p. 129—131 °C (from pentane–diethyl ether) (Found: C, 70.4; H, 6.6. $C_{20}H_{22}O_3S$ requires C, 70.2; H, 6.5%); $\lambda_{max.}$ 247 nm (log ε 4.0); $\nu_{max.}$ 1 767 (acetate CO), 1 715 (acetylthio CO), and 1 175 cm^{-1} (C–O); δ_H 1.40 (s, CMe_3), 2.28 (s, SCOMe), 2.33 (OCOMe), and 7.15—7.62 (m, ArH); *m*/*z* 342 ($M^{+\cdot}$), 300, 258, 243, and 43.

(c) *In* Et_2O–BF_3·Et_2O. Boron trifluoride–diethyl ether (0.5 ml, 4 mmol) was added to a solution of the *p*-quinol (2) (430 mg, 0.144 mmol) in dry diethyl ether (3 ml). The red-violet solution was kept at room temperature for 7 h and then diluted with diethyl ether. Work-up, followed by p.l.c., gave: (i) the 1,1'-biphenyl-4-ol (16) (104 mg, 26%); (ii) 2-*methyl*-6-*phenyl*-4-*t*-*butyl*-1,3-*benzodioxole* (43) (79 mg, 20%), m.p. 55—57 °C (from MeOH) (Found: C, 80.8; H, 7.4. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%), $\lambda_{max.}$ 282 (log ε 4.09) and 265 nm (4.22); $\nu_{max.}$ 1 211 cm^{-1} (C–O); δ_H 1.40 (s, CMe_3), 1.67 (d, *J* 5 Hz, Me), 6.15 (q, *J* 5 Hz, CH_3CH=), 6.73 (d, *J* 1 Hz, 5-H), 6.82 (d, *J* 1 Hz, 7-H), and 7.05—7.47 (m, ArH); *m*/*z* 268 ($M^{+\cdot}$) and 253; δ_C 20.8 (Me), 29.3 (CMe_3), 34.0 (CMe_3), 105.4 (C-2), 108.6 (C-7), 117.9 (C-5), 126.6 (C-4'), 126.9 (C-2' and C-6'), 128.6 (C-3' and C-5'), 132.5 (C-4), 134.7 (C-6), 141.5 (C-1'), 144.7 (C-3a), and 148.2 p.p.m. (C-7a); and (iii) 4-(2-methylprop-2-enyl)-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone (42) (85 mg, 18%).

Repetition of the reaction in the dark or in the presence of galvinoxyl gave the same results.

Addition of t-butyl alcohol (45 mg, 0.61 mmol) to a solution of the *p*-quinol (2) (78 mg, 0.26 mmol) and BF_3·Et_2O (0.16 ml, 1.27 mmol) in diethyl ether (1 ml) gave, after 5 h at room temperature, the compounds (16), (42), and (43) in the ratio (^{1}H n.m.r.) 31 : 38 : 31.

(d) *In* MeOH–$HClO_4$. A solution of the *p*-quinol (2) in anhydrous methanol (1 ml) was treated with perchloric acid (70% aqueous; 3 drops). After 24 h at room temperature work-up, followed by p.l.c. (hexane–diethyl ether, 19 : 1), gave: (i) the 1,1'-biphenyl-4-ol (16) (15 mg, 13%); (ii) 4-methoxy-4-phenyl-2,6-di-t-butylcyclohexa-2,5-dienone [4] (8) (64 mg, 49%); (iii) 5-methoxy-3-t-butyl-1,1'-biphenyl-4-ol [4] (20) (9 mg, 8%); and (iv) the *o*-benzoquinone (37) (5 mg, 5%).

(e) *In* Et_2O–$HClO_4$, CH_2Cl_2–CF_3SO_3H, *or* $MeNO_2$–CF_3SO_3H. The related couple, biphenyl-4-ol (16) and *o*-benzoquinone (37), were the only products detected from these media.

Synthesis of 2-*Methyl*-6-*phenyl*-4-*t*-*butylbenzo*-1,3-*dioxole* (43).—A mixture of 5-t-butyl-1,1'-biphenyl-3,4-diol (22) (62 mg, 0.26 mmol), vinyl acetate (60 mg, 0.72 mmol), mercury(II) oxide (1 mg), and boron trifluoride–diethyl ether (5 mg) was stirred in toluene (1 ml) at room temperature under nitrogen for 24 h. Work-up and p.l.c. gave the dioxole (43) (28 mg, 40%), identical with the sample isolated above.

Rearrangement of 4-*Hydroxy*-4-*phenyl*-2-*t*-*butylcyclohexa*-2,5-*dienone* (5).—A solution of concentrated sulphuric acid (5 mg, 0.05 mmol) in acetic anhydride (3 ml) was added dropwise to a stirred solution of the mono-t-butyl-*p*-quinol (5) (420 mg, 1.7 mmol) in acetic anhydride (15 ml) at 0 °C. After 30 min work-up, followed by p.l.c., gave ten bands, one of which was starting material (72 mg). The only product recovered in a pure state was 3-*t*-*butyl*-1,1'-*biphenyl*-4-*ol* (25) (45 mg, 20%), b.p. 80 °C at 0.07 mmHg (Found: C, 85.6; H, 8.1. $C_{16}H_{18}O$ requires C, 84.90; H, 8.0%), δ_H 1.45 (s, CMe_3), 4.67 (s, exchangeable on deuteriation, OH), 6.55 (d, *J* 7 Hz, 5-H), and 7.30 (m, ArH). This phenol was identical with the compound synthesized by reduction of the *p*-quinol (5) with zinc and concentrated hydrochloric acid in 1,2-dimethoxyethane.

Use of concentrated sulphuric acid (1 drop) and the *p*-quinol (5) (190 mg) in acetic anhydride (3 ml) at room temperature for 3.5 h similarly afforded a complex mixture. The only product obtained in a pure state was 3-*t*-*butyl*-1,1'-*biphenyl*-4-*yl acetate* (24) (37 mg, 19%), m.p. 82—83 °C (Found: C, 80.6; H, 7.6. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%), $\lambda_{max.}$ 248 nm (log ε 3.60); $\nu_{max.}$ 1 762 cm^{-1} (OAc); δ_H 1.40 (s, CMe_3), 2.28 (s, OAc), 6.95 (d, *J* 7 Hz, 5-H), and 7.22—7.63 (m, ArH); *m*/*z* 268.1453 ($M^{+\cdot}$; $C_{18}H_{20}O_2$ requires 268.1442), 226, 211, and 183. Treatment of the phenol (25) with acetic anhydride–pyridine also afforded the acetate (24).

Rearrangement of 4-*Hydroxy*-2,6-*dimethyl*-4-*phenylcyclohexa*-2,5-*dienone* (6).—A mixture of the *p*-quinol (6) (193 mg, 0.9 mmol) and concentrated sulphuric acid (3 drops) in acetic anhydride (2 ml) was kept at room temperature for 24 h. Work-up, followed by p.l.c. (hexane–diethyl ether, 3 : 1), gave: (i) 3,5-dimethyl-1,1'-biphenyl-4-yl acetate (26) (13 mg, 6%), m.p. 99—105 °C (from ether), $\lambda_{max.}$ 248 nm (log ε 3.89); $\nu_{max.}$ 1 765 and 1 210 cm^{-1} (aromatic OAc); δ_H 2.20 (s, Me), 2.30 (s, OAc), and 7.08—7.57 (m, ArH); *m*/*z* 240 ($M^{+\cdot}$) and 198; and (ii) 3,5-*dimethyl*-1,1'-*biphenyl*-2,4-*diyl diacetate* (47) (171 mg, 64%), m.p. 98—100 °C (from pentane–diethyl ether) (Found: C, 72.4; H, 6.2. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.1%), $\lambda_{max.}$ 240 nm (log ε 4.18); $\nu_{max.}$ 1 760 and 1 200 cm^{-1} (aromatic OAc); δ_H 1.92 (s, Me), 1.95 (s, Me), 2.13 (s, OAc), 2.25 (s, OAc), 6.97 (s, 6-H), and 7.28 (s, ArH); *m*/*z* 298 ($M^{+\cdot}$), 256, and 214; δ_C 10.5 (Me at C-5), 16.2 (Me at C-3), 20.4 (OCOMe), 123.8 (C-3), 127.3 (C-6), 128.0 (C-5), 128.1 (C-2' and C-6'), 128.8 (C-3' and C-5'), 129.5 (C-4'), 132.7 (C-1), 137.6 (C-1'), 145.0 (C-2), 147.7 (C-4), 168.4 (OCOMe), and 168.6 p.p.m. (OCOMe).

Rearrangement of 4-*Hydroxy*-2,6-*di*-*isopropyl*-4-*phenylcyclohexa*-2,5-*dienone* (4).—A solution of the *p*-quinol (4) (50 mg, 0.19 mmol) in acetic anhydride (0.7 ml) and concentrated sulphuric acid (1 drop) was kept at room temperature for 24 h, and then poured onto ice. The crude product was subjected to p.l.c. (hexane–diethyl ether, 3 : 1) to give: (i) 4-acetoxy-3,5-di-isopropyl-1,1'-biphenyl (27) (5 mg, 9%), $\lambda_{max.}$ 233 nm (log ε 4.17); $\nu_{max.}$ 1 760 cm^{-1} (OAc); δ_H 1.22 (d, *J* 7 Hz, $CHMe_2$), 2.32 (s, OAc), 2.90 (sp, *J* 7 Hz, $CHMe_2$), and 7.17—7.62 (m, ArH); *m*/*z* 296 ($M^{+\cdot}$), 254, and 239; and (ii) 3,5-*di*-*isopropyl*-1,1'-*biphenyl*-2,4-*diyl diacetate* (49) (25 mg, 37%), m.p. 105—107 °C (from pentane–diethyl ether) (Found: C, 74.3; H, 7.6. $C_{22}H_{20}O_4$ requires C, 74.6; H, 7.4%), $\lambda_{max.}$ 232 nm (log ε 4.28); $\nu_{max.}$ 1 760 cm^{-1} (aromatic

OAc); δ_H 1.22 (d, *J* 7 Hz, CH*Me*$_2$) 1.87 (s, OAc at C-2), 2.30 (s, OAc at C-4), 2.92 (sp, *J* 7 Hz, C*H*Me$_2$), 6.98 (s, 6-H), and 7.25 (s, ArH); *m/z* 354 ($M^{+\cdot}$), 312, 270, and 255.

Acid-catalyzed Reactions of 4-Hydroxy-4-methyl-2,6-di-t-butylcyclohexa-2,5 dienone (7).—(a) *In* Ac_2O–H_2SO_4. Concentrated sulphuric acid (3 drops) was added to a solution of the *p*-quinol (250 mg, 1.06 mmol) in acetic anhydride (2 ml). The mixture was kept at room temperature for 24 h. Work-up, followed by p.l.c. (hexane–diethyl ether, 3 : 1), gave: (i) 4-acetoxy-3,5-di-t-butylbenzyl acetate (29) (153 mg, 45%), b.p. (Kugelrohr) 130—130.5 °C at 0.2 mmHg (lit.,[29] 166—168 °C at 7 mmHg) (Found: C, 71.0; H, 8.9. Calc. for $C_{19}H_{28}O_4$: C, 71.2; H, 8.8%), $\lambda_{max.}$ 262 nm (log ε 1.70); $\nu_{max.}$ 1 742 (aromatic OAc) and 1 730 cm^{-1} (benzylic OAc); δ_H 1.33 (s, CMe_3), 2.05 (s, OAc), 2.27 (s, OAc), 4.98 (s, Ph*Me*), and 7.20 (s, ArH); *m/z* 320 ($M^{+\cdot}$), 278, and 263; δ_C 21.0 (OCO*Me*), 22.6 (OCO*Me*), 31.4 (C*Me*$_3$), 35.4 (*C*Me$_3$), 66.5 (Ph*C*H$_2$), 126.6 (C-2 and C-6), 132.7 (C-1), 142.7 (C-3 and C-5), 147.9 (C-4), and 170.8 p.p.m. (*O*COMe); and (ii) 4-hydroxymethyl-2,6-di-t-butylphenyl acetate (28) (16 mg, 5%), m.p. 98—100 °C (from hexane) (Found: C, 73.2; H, 9.6. $C_{17}H_{26}O_3$ requires C, 73.4; H, 9.4%), $\lambda_{max.}$ 261 nm (log ε 2.00); $\nu_{max.}$ 3 450 (OH) and 1 758 cm^{-1} (aromatic OAc); δ_H 1.33 (s, CMe_3), 1.68 (s, exchangeable on deuteriation, OH), 2.27 (s, OAc), 4.40 (s, PhC*H*$_2$), and 7.15 (s, ArH); *m/z* 278 ($M^{+\cdot}$), 236, and 229.

A reaction quenched after 1 h gave only the benzylic acetate (29) (62%); ^{1}H n.m.r. analysis of the crude product showed no benzylic alcohol (31).

(b) *In* HOAc–H_2SO_4. A solution of concentrated sulphuric acid (1 drop) in acetic acid (0.1 ml) was added to a solution of the *p*-quinol (7) (97 mg, 0.41 mmol) in acetic acid (1.5 ml). After 24 h work-up ^{1}H n.m.r. analysis showed the product to be mainly 4-hydroxy-3,5-di-t-butylbenzyl acetate,[29] δ_H 1.43 (s, CMe_3), 2.00 (s, OAc), 4.90 (s, CH_2OAc), 5.12 (s, exchangeable on deuteriation, OH), and 7.05 (s, ArH).

(c) *In* Et_2O–BF_3·Et_2O. A solution of BF_3·Et_2O (1 drop) in dry diethyl ether (0.1 ml) was added to a solution of the *p*-quinol (7) (266 mg, 0.89 mmol) in dry diethyl ether (1 ml). After 24 h, p.l.c. of the crude product gave: (i) 4-(3,5-*di-t-butyl-4-hydroxybenzyloxy*)-4-*methyl*-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (51) (160 mg, 79%), b.p. 164 °C at 0.4 mmHg (Found: C, 79.2; H, 10.0. $C_{30}H_{46}O_3$ requires C, 79.2; H, 10.2%), $\lambda_{max.}$ 273 (log ε 3.74) and 225 nm (4.17); $\nu_{max.}$ 3 645 (OH), 1 667, and 1 645 cm^{-1} (conjugated CO); δ_H 1.22 [s, C(Me)$_3$], 1.45 (s, CMe_3 on aryl ring, and Me), 4.08 (s, CH_2O), 4.95 (s, exchangeable on deuteriation, OH), 6.37 (s, 3-H and 5-H), and 6.88 (s, ArH); *m/z* 454 ($M^{+\cdot}$), 412, 235, 220, 219, 205, 164, 149, and 57; and (ii) starting material (53 mg, 20%).

(d) *In* THF–$HClO_4$. Perchloric acid (60% aqueous, 3 drops) was added to a solution of the *p*-quinol (7) (188 mg, 0.8 mmol) in THF (1 ml). After 48 h at room temperature, the solution was partitioned between diethyl ether and saturated aqueous sodium hydrogen carbonate. The organic layer was concentrated and the residue was subjected to p.l.c. (hexane–diethyl ether, 19 : 1) to give: (i) the unsymmetrical dimer (51) (40 mg, 22%); (ii) *bis*(4-*hydroxy*-3,3-*di-t-butylbenzyl*) *ether* (52) (30 mg, 17%), m.p. 133—134 °C (from MeOH–H_2O) (Found: C, 79.0; H, 9.9. $C_{30}H_{46}O_3$ requires C, 79.2; H, 10.2%), $\lambda_{max.}$ 223 nm (log ε 3.80); $\nu_{max.}$ 3 650 cm^{-1} (OH); δ_H 1.48 (s, CMe_3), 4.35 (s, ArC*H*$_2$), 4.97 (s, exchangeable on deuteriation, OH), and 7.02 (s, ArH); *m/z* 454 ($M^{+\cdot}$), 221, 220, 219, 164, 163, and 57; (iii) starting material (57 mg, 30%); and (iv) 4-hydroxy-3,5-di-t-butylbenzyl alcohol (31) (10 mg, 5%), m.p. 140—145 °C (from MeOH) (lit.,[33] 140—141 °C), $\lambda_{max.}$ 271 nm (log ε 2.77); $\nu_{max.}$ 3 650 cm^{-1} (OH); δ_H 1.45 (s, CMe_3), 4.45 (s, ArC*H*$_2$), 5.02 (s, exchangeable on deuteriation, OH), and 7.03 (s, ArH); *m/z* 236 ($M^{+\cdot}$) and 221.

(e) *1,2-Dimethoxyethane–Nafion H*. A mixture of the *p*-quinol (7) (106 mg, 0.50 mmol) and Nafion-H [30] in 1,2-dimethoxyethane (1 ml) was stirred at room temperature for 24 h. Decantation of the solution, concentration of the solution, and p.l.c. (hexane–diethyl ether, 9 : 1) of the residue gave: (i) 4,4′-methylenebis(2,6-di-t-butylphenol) (53) (14 mg, 5%) m.p. 151—154 °C (from MeOH) (lit.,[31] 154—156 °C), $\lambda_{max.}$ 273 (log ε 4.03) and 232 nm (4.62); $\nu_{max.}$ 3 650 cm^{-1} (OH); δ_H 1.42 (s, CMe_3), 3.73 (s, CH_2), 4.88 (s, exchangeable on deuteriation, OH), and 6.82 (s, ArH); *m/z* 424 ($M^{+\cdot}$), 409, 367, and 219; (ii) the unsymmetrical dimer (51) (18 mg, 6%); (iii) the symmetrical dimer (52) (41 mg, 13%); (iv) starting material (16 mg, 10%); and (v) the monomeric benzyl alcohol (31) (19 mg, 12%).

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