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Oxidation of Bisphenols. II*
Some Compounds Related to Galvinoxyl

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Abstract

The oxidation of a series of 4,4′-alkylidenebis(2,6-di-t-butylphenols) having increasing substitution of the central methylene carbon by alkyl groups is examined. In the monosubstituted compounds the stability of the monophenoxy radical increases with increase in the size of the substituent, while the stability of the galvinoxyl type radical decreases. β-Coupled products are only obtained from the ethylidene bisphenol, a result that can be correlated with e.s.r. hyperfine splitting constants. With increasing mono- or di-substitution bisspiroperoxides become the preferred oxidation products. The e.s.r. spectrum of an ethylenebisgalvinoxyl biradical is described.

Introduction

Interest in sterically hindered alkylidenebisphenols stems both from their oxidation to stable free radicals, e.g. galvinoxyl (12)[1,2] and from their efficient inhibition of autoxidation at relatively high temperatures.[3] The use of these compounds as antioxidants makes it desirable to determine their oxidation products. In this we have studied the effect of increasing alkyl substitution of the central methylene carbon. The oxidants used were chiefly potassium ferricyanide and silver oxide, and the bisphenol compounds (1), (2), (3), (4), (6) and (7). The products obtained are shown in Table 1, and for comparative purposes previously[1,2,4,5] identified oxidation products of bisphenols (1) and (5) have been included. Following Table 1 we present evidence on which the structures of the products are based, and the last part of the discussion is devoted to an attempt to correlate the formation of these products with the degree of substitution of the central methylene carbon, and with e.s.r. spectra of radicals observed during the oxidations.

Structural Assignments

Quinonemethides (8)–(11)

Of these the structure of (8) has already been established.[2] The n.m.r. spectra of these compounds include signals for the two equivalent ring protons and the 18

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* Part I, *Aust. J. Chem.*, 1975, **28**, 343.

[1] Joshi, B. S., *Chem. Ind. (London)*, 1957, 525.

[2] Coppinger, G. M., *J. Am. Chem. Soc.*, 1957, **79**, 501.

[3] Prusikova, M., Jirackova, L., and Pospisil, J., *Collect. Czech. Chem. Commun.*, 1972, **37**, 3788.

[4] Kharasch, M. S., and Joshi, B. S., *J. Org. Chem.*, 1957, **22**, 1435.

[5] Chandross, E. A., and Kreilick, R., *J. Am. Chem. Soc.*, 1963, **85**, 2530; see also Becker, H.-D., *J. Org. Chem.*, 1967, **32**, 2115, 2136 for (5; $R^1 = R^2 =$ Ph) and (33; $R^1 = R^2 =$ Ph).

equivalent t-butyl protons of the aromatic ring, as well as pairs of 9-proton singlets for the non-equivalent t-butyl groups and an AB quartet (*J* c. 2·5 Hz) for the non-equivalent protons of the cyclohexadienone ring. Molecular non-equivalence of this type has previously been observed in stilbenequinones[6] and indophenols,[7] as well as in simpler quinonemethides,[8] and has been explained by Dyall and Winstein.[9] The infrared spectra of these compounds exhibit typical absorptions in the carbonyl–alkene region (Table 2), as well as hindered hydroxyl absorption at 3645 cm^{-1}.

Table 1. Oxidation products isolated

Bisphenol	Oxidant	Products
(1)	$K_3Fe(CN)_6/N_2$	(12)[1]
	PbO_2/N_2	(12)[2]
	O_2/base	(8), (23), (24)[4]
	Ag_2O/N_2	(12)
	Ag_2O/air	(16)
	$K_3Fe(CN)_6$/air	(8), (16), (23), (24), (25), (26)
(2)	4 equiv. $K_3Fe(CN)_6$/air/4 min	(17), (23), (25), (27), (28)
	excess $K_3Fe(CN)_6$/air/ > 30 min	(17), (23), (25), (29)
	1 equiv. Ag_2O/air	(23), (28)
	> 2 equiv. Ag_2O/N_2	(9), (17), (23), (25), (29), (30)
	aged Ag_2O or MnO_2/N_2	[(2), (9)] complex
	$PbO_2/N_2/C_6H_6$ reflux/ > 24 h	(23), (28), (31), (32)
(3)	4 equiv. $K_3Fe(CN)_6/N_2$	(10), (18), (23), (25)
	Ag_2O/N_2	(10), (18), (23), (25)
(4)	4 equiv. $K_3Fe(CN)_6/N_2$/ > 10 h	red complex+(19), (23), (25)
	Ag_2O/N_2	red complex+(19), (23), (25), (27)
(5)	$K_3Fe(CN)_6/N_2$	(33)[5]
	Ag_2O, PbO_2, or MnO_2/N_2	(33)[5]
	these oxidants in air	(20)[5]
(6)	Ag_2O/N_2/24 h	(21), (23)
(7)	Ag_2O/O_2/6 h	(22)
	Ag_2O/N_2/24 h	(22), (23)

Table 2. Carbonyl and alkene i.r. absorption frequencies for quinonemethides (CCl_4)

Compound	Wavenumbers (cm^{-1})	Compound	Wavenumbers (cm^{-1})
(9)	1660w, 1646m, 1634m, 1613s	(29)	1651s, 1638m, 1613w
(10)	1665w, 1647m, 1635m, 1615s	(30)	1654s, 1632w, 1618s
(11)	1665w, 1647m, 1634m, 1614s	(35)	1652s, 1643m, 1613w
(26)	1642w, 1631m, 1609s	(32)	1642w, 1625m, 1604s
(28)	1640m, 1630m, 1600s		

Cyclic Peroxides (16)–(22)

Compound (20) has already been described.[5] All show a pronounced (M − 32) peak in the mass spectrum. Where the methylene group of the peroxide ring is

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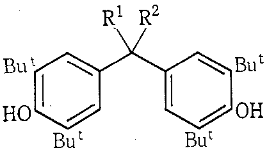
[6] Brownstein, S., and Ingold, K. U., *J. Am. Chem. Soc.*, 1962, **84**, 2258.

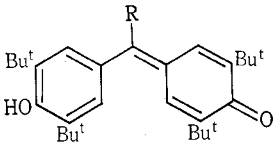
[7] Coppinger, G. M., and Jungnickel, *J. Chem. Phys.*, 1963, **38**, 2589.

[8] Kessler, H., and Rieker, A., *Tetrahedron*, 1968, **24**, 5133.

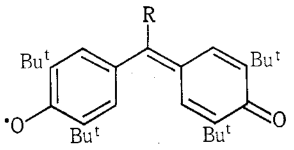
[9] Dyall, L. K., and Winstein, S., *J. Am. Chem. Soc.*, 1972, **94**, 2196.



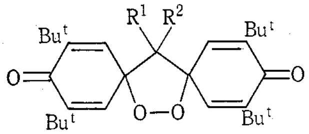
	R^1	R^2
(1)	H	H
(2)	Me	H
(3)	Et	H
(4)	Pr^i	H
(5)	Me	Me
(6)	Et	Me
(7)	—$(CH_2)_5$—	



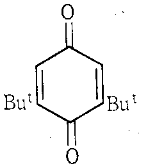
	R
(8)	H
(9)	Me
(10)	Et
(11)	Pr^i



	R
(12)	H
(13)	Me
(14)	Et
(15)	Pr^i



	R^1	R^2
(16)	H	H
(17)	Me	H
(18)	Et	H
(19)	Pr^i	H
(20)	Me	Me
(21)	Et	Me
(22)	—$(CH_2)_5$—	



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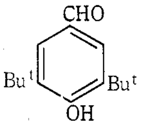

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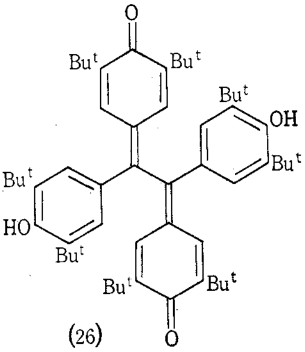

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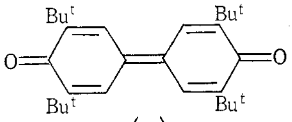

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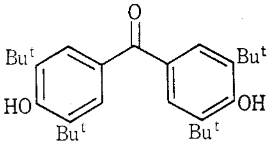

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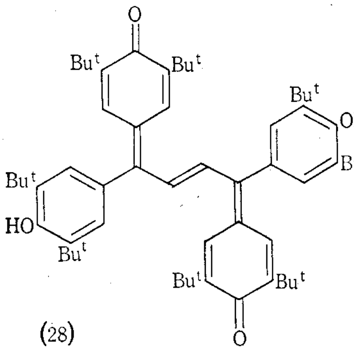

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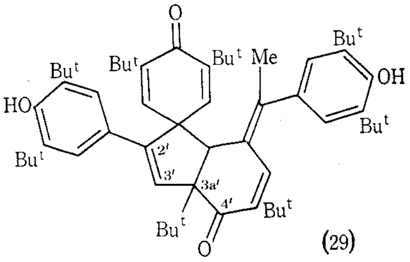

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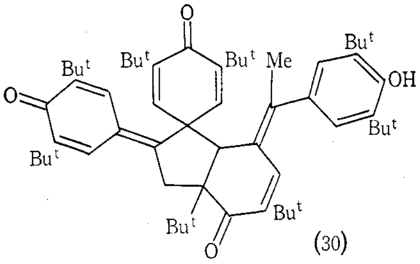

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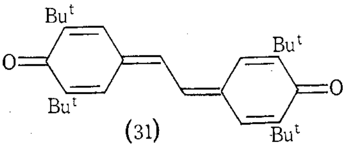

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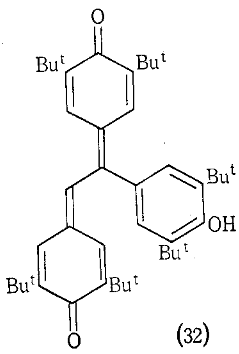

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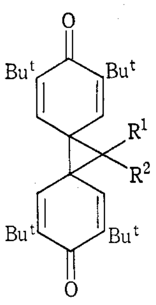


	R^1	R^2
(33)	Me	Me
(37)	H	Pr^i

unsymmetrically substituted the cyclohexadienone ring substituents exhibit non-equivalence in the n.m.r. spectrum.

Bisquinonemethide (26)

This compound has been previously described.[10] Hydrogenation required two equivalents of hydrogen and gave the corresponding tetrakisphenol, which proved identical to a sample prepared by Ullmann condensation of the bromo(diphenyl)methane.

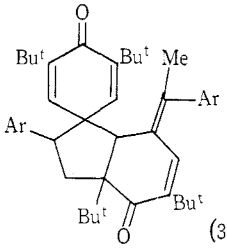
Bisquinonemethide (28)

Combustion analysis and mass spectrometry established the molecular formula of $C_{60}H_{84}O_4$. A pronounced (M+2) ion was observed. The n.m.r. spectrum showed resonances that were comparable with those of the stilbenequinone (31), showing non-equivalence, and another set comparable with those of 4,4′-ethenediylbis-(2,6-di-t-butylphenol). The infrared spectrum, besides showing hindered hydroxyl absorption, was also characteristic of a quinonemethide (Table 2). On hydrogenation three equivalents of hydrogen were absorbed, the product being the tetrakisphenol (34), which had *m/e* 874. The n.m.r. spectrum of (34) was consistent with a molecule of higher symmetry, showing singlets for the hydroxyl, t-butyl, and ring protons, with a two-proton triplet and a four-proton doublet confirming the nature of the bridge.

$Ar_2CHCH_2CH_2CHAr_2$ (34) (Ar = 3,5-di-t-butyl-4-hydroxyphenyl both here and in subsequent formulae)

Dimers (29) and (30)

The dimer (29), the major oxidation product of (2), was also produced in small and variable yield by oxidation of the quinonemethide (9). The dimer (30) was only obtained by careful crystallization of the silver oxide oxidation product of bisphenol (2). Absorption on alumina was sufficient to change (30) into (29). The relationship between these two compounds was further demonstrated when they both afforded the same dihydro compound (35) on hydrogenation. Thus compound (30) is the true oxidation product of (2) and compound (29) an artefact produced during the chromatographic separation. Although it was possible to predict most of the structural features of these three compounds from spectroscopic data, final confirmation was only obtained after X-ray crystallographic analysis of (29), which is reported in an accompanying paper.[11] The isomerization of quinonemethides to alkenylphenols by alumina has been noted previously.[12]



(35)

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[10] Chandross, E. A., *J. Am. Chem. Soc.*, 1964, **86**, 1263.

[11] Hall, S. R., Raston, C. L., and White, A. H., *Aust. J. Chem.*, 1980, **33**, 295.

[12] Braun, D., and Meier, B., *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 566.

In the n.m.r. spectrum of (30), instead of the vinylic H 3 singlet at δ 6·34 observed for compound (29), there are two one-proton doublets at 2·71 and 3·99. By decoupling these were assigned to the geminal protons at C 3 of compound (30). In the reduced compound (35) these protons are again coupled to that at C 2. The ^{13}C n.m.r. spectrum of compound (29) showed two carbonyl and two phenolic carbons, while that of (30) showed an increase of one carbonyl at the expense of one phenolic carbon resonance. In both spectra the resonance at lowest field was assigned to C 4, since the chemical shift of the carbonyl carbon decreases with increasing conjugation.[13] This is also in accord with the deviation from planarity of the indane system revealed crystallographically.[11] Carbonyl–alkene i.r. frequencies for compounds (29), (30) and (35) are also recorded in Table 2, although they are of course composite bands.

Quinonemethide (32)

Evidence for this structure comes from the mass spectrum, requiring a molecular formula of $C_{44}H_{62}O_3$, and the absorption of two equivalents of hydrogen to give the trisphenol (36). The mass spectrum of the latter shows two notable fragment ions at *m/e* 219 and 423 due to loss of the 3,5-di-t-butyl-4-hydroxybenzyl ion. The n.m.r. spectra fully support structures (32) and (36).

Ar_2CHCH_2Ar
(36)

The Complex from Bisphenol (2)

Oxidation of bisphenol (2) with silver oxide or manganese dioxide under mild conditions gave an orange material as the major product. This crystallized directly from the crude oxidation product. Its spectroscopic properties were consistent with those of a mixture of the bisphenol (2) and the quinonemethide (9). On hydrogenation only the bisphenol (2) was obtained. We conclude that this compound is a charge transfer complex of the quinhydrone type.

The Complex from Bisphenol (4)

Crystallization of the crude oxidation product of bisphenol (4) gave a red solid as the major product. Its n.m.r. spectrum consisted only of a very broad signal at high field. In the solid state it exhibited an e.s.r. spectrum consisting of a broad singlet, but a solution in deoxygenated benzene gave a doublet (*a* 0·246 mT) of triplets (*a* 0·165 mT). The same e.s.r. spectrum was obtained on oxidation of the bisphenol (4). This is consistent with the phenoxy radical (15), and will be further discussed later.

Hydrogenation of this paramagnetic material afforded only the bisphenol (4). Its mass spectrum had *m/e* 264, which is two units less than that of the bisphenol. In the solid form the material was stable for many months, but in solution it decomposed. Solutions in light petroleum or ethanol became yellow in air and afforded the spiroperoxide (19) in almost quantitative yield. The infrared spectrum of solutions of the red material did not show hydroxyl absorption, but bands were observed at 1670, 1640 and 1620 cm^{-1}. These last two are comparable with bands at 1643 and 1621 cm^{-1} observed for the cyclopropane (33),[5] and suggest the presence of the cyclopropane (37), at least in part. However, we were unable to isolate this compound,

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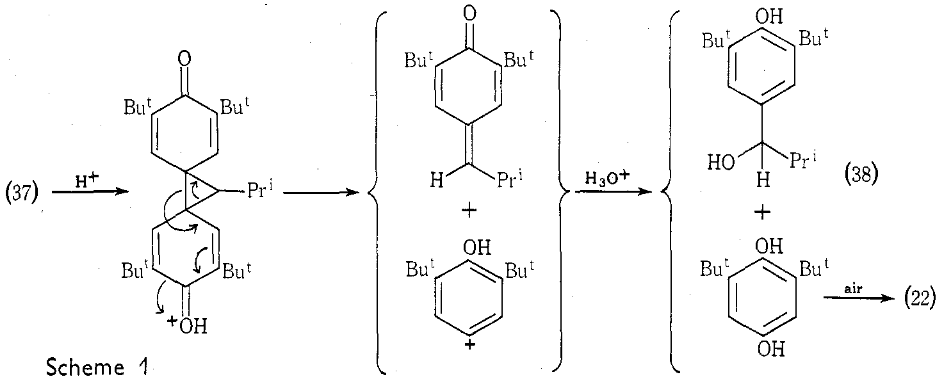
[13] Marr, D. H., and Stothers, J. B., *Can. J. Chem.*, 1965, **43**, 596.

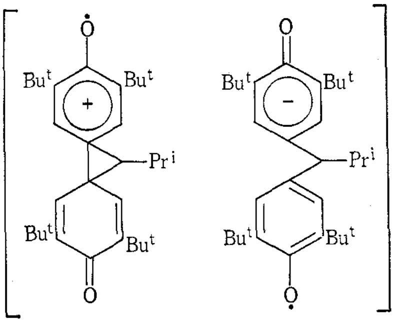
or to observe by e.s.r. the biradical with which it should be in equilibrium. Another broad band at 1550 cm^{-1} is assigned to the C–O stretching absorption of the phenoxyl oxygen of the radical (15).[5,14] The ultraviolet spectrum (cyclohexane) showed absorption at 205, 256 and 327 nm, tailing off into the visible region, as does that of (33).



Scheme 1

When dissolved in acetic acid the red material decomposed almost immediately to a mixture of the benzoquinone (22) (20–40%) and the benzyl alcohol (38) (30–55%). The identity of the latter was established by acylation of 2,6-di-t-butylphenol with 2-methylpropionyl chloride followed by reduction. The formation of these two products (22) and (38) from the cyclopropane (37) can be rationalized as in Scheme 1.

We suggest that the red material is a charge transfer complex, one form of which can be represented as (39), which dissociates in solution to the biradical/cyclopropane (37), and then reacts with oxygen to give the peroxide (19).



(39)

E.S.R. Spectra

The radicals whose splitting constants are shown in Table 3 were prepared by oxidizing the bisphenols with silver oxide in degassed benzene. The immediate signal was that of the monophenoxy radical, which changed, increasingly slowly with increasing substitution of the methylene carbon, to that of the galvinoxyl type (12)–(15) in those compounds containing a methylene hydrogen. The latter radicals were also produced by oxidation of the corresponding quinonemethides (8)–(11).

Because of the similarity of the splittings produced by the *meta* protons in the monophenoxy radicals, it is clear that any changes in reactivity must be related to variations in the ease with which the unpaired electron can be delocalized to the

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[14] Altwicker, E. R., *Chem. Rev.*, 1967, **67**, 475.

Table 3. Hyperfine splitting constants (mT) of monophenoxy radicals and galvinoxyl type radicals in benzene

Multiplicities are given in parentheses

Bisphenol	Monophenoxy radical		Galvinoxyl type radical	
(1)	0·906 (3),	0·16 (3)	0·586 (2),	0·138 (5)[B]
(2)	0·59 (2),	0·17 (3)	0·247 (4),	0·11 (5)
(3)	0·415 (2),	0·165 (3)	0·125 (3),	0·125 (5)
(4)	0·265 (2),	0·16 (3)	unres.,	0·125 (5)
(5)		0·162 (3)		
(6)		0·166 (3)		
(7)		0·165 (3)		
(1)[A]		0·167 (3)		
(28)			0·21 (2),	0·13 (5)
(29)	0·48 (2),	0·166 (3)		
(30)		0·18 (3)		

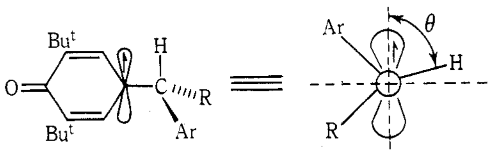
[A] (1; $R^1 = R^2 = Ph$).

[B] Gierke, W., Harrer, W., Kirste, B., Kurreck, H., and Reusch, J., *Z. Naturforsch., Teil B.*, 1976, **31**, 965, give the values 0·583 and 0·134 mT.

Table 4. Hyperfine splitting constants (mT) for some 4-substituted 2,6-di-t-butylphenoxy radicals in benzene

Multiplicities in parentheses. Some of these radicals have been described previously, but were reprepared for this comparison

4-Substituent	Ring protons	β-Protons	γ-Protons
Me	0·153 (3)	1·032 (4)	
Et	0·155 (3)	0·848 (3)	
Pr	0·155 (3)	0·765 (3)	
CH_2CHMe_2	0·162 (3)	0·696 (3)	0·056 (2)
c-C_6H_{11}	0·159 (3)	0·453 (2)	0·049 (5)
CH_2Ph	0·166 (3)	0·908 (3)	
CHMePh	0·173 (3)	0·653 (2)	
$CHPh_2$	0·165 (3)	0·829 (2)	



(40)

benzylic proton. This hyperconjugation has been shown to be closely dependent upon the position of the benzylic (or β) proton relative to the ring,[15] and this has been expressed as

$$a_\beta^{\mathrm{H}} = (B_0 + B\cos^2\theta)\rho_\alpha$$

by Heller and McConnell.[16] As the substituents R and Ar of (40) become more

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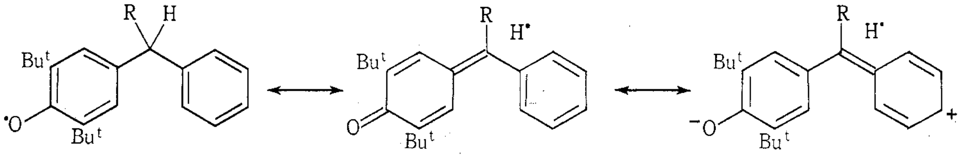
[15] Lykos, P. G., *J. Chem. Phys.*, 1960, **32**, 625.

[16] Heller, C., and McConnell, H. M., *J. Chem. Phys.*, 1960, **32**, 1535.

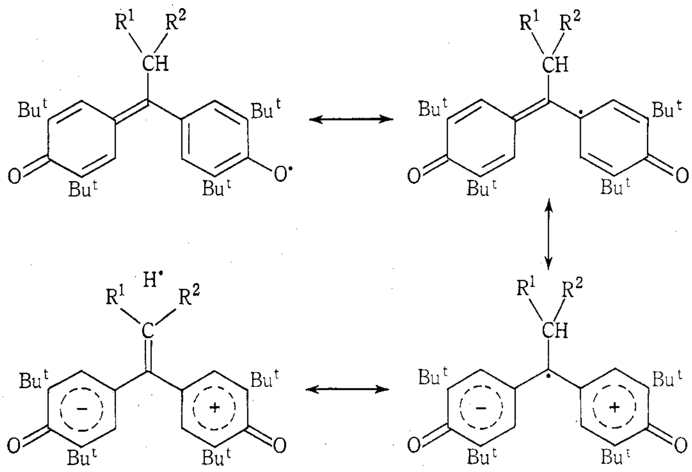
bulky and increasingly interfere with the *meta* ring protons, conformations in which R and Ar experience less steric hindrance become favoured, and the dihedral angle θ between the benzylic proton and the π orbital system of the adjacent ring increases, thus reducing a_β^H.

This is clearly demonstrated in the series of 4-substituted 2,6-di-t-butylphenoxy radicals shown in Table 4. It can also be seen that changing R from Me to Ph increases a_β^H. This apparent contradiction is explicable in terms of the extra stability given to the hyperconjugated resonance form by conjugation with the phenyl group as in Scheme 2. This requires the rings to be coplanar, with a consequent decrease in θ and increase in a_β^H.



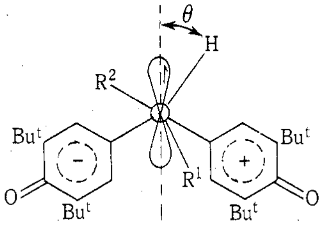
Scheme 2

The overall extent to which the monophenoxy radicals derived from (1)–(4) can be delocalized by hyperconjugation of the β-proton thus decreases as the bulk of R increases. It is also apparent that the decreasing coplanarity of the rings reduces the stability of the galvinoxyl type radical to which the monophenoxy radical can be further oxidized. The relative stability of the monophenoxy radical is shown by the time required for the initial e.s.r. spectrum to start to change. These times were approximately for (1) a few minutes, (2) 30 min, (3) 5 h and (4) 10 h. Where there is no possibility of forming a galvinoxyl type radical, as in bisphenols (5)–(7), the primary radicals also show considerable stability, demonstrated by reduction after several hours to the parent bisphenol by the addition of hydroquinone. This progressive increase in the stability of the monophenoxy radical not only explains the increasing preponderance of spiroperoxide formation, but also suggests that it is a monoradical which reacts with oxygen (see Scheme 4 below) rather than a biradical.



Scheme 3

The e.s.r. spectra of the galvinoxyl radicals (12)–(15) show decreasing delocalization of the unpaired electron to the β-carbon atom with increasing size of the substituent R. Again a hyperconjugative mechanism is probably involved as shown in Scheme 3. The dependence of this hyperconjugation on the dihedral angle θ can be seen in (41).



(41)

Where R^1 and R^2 are both protons, as in (13), there is negligible steric interaction and the methyl group can rotate freely. This results in a time dependent average angle θ of 45°. From the simplified relationship

$$a_\beta^{\mathrm{H}} \propto \cos^2\theta$$

and the splitting constants of Table 3 approximate values of θ for the galvinoxyls (14) and (15) can be calculated as 60° and 90° respectively. Thus, the higher delocalization of the unpaired electron onto the β-carbon atom in radical (13) may explain why β-coupled products were obtained only from the bisphenol (2).

E.s.r. spectra were also obtained on oxidation of several of the products, and are included in Table 3. The one (Fig. 1) from the bisquinonemethide (28) is of particular interest in showing that the unpaired electron is confined to one half of the molecule, the doublet splitting being assigned to one proton of the central double bond. It should therefore be possible to observe a biradical derived from (28), as the e.s.r. spectrum of the biradical bisgalvinoxyl has been observed on oxidizing the bisquinonemethide (26).[10] The configuration of the central double bond is assumed to be *E* on steric grounds. This finding is supported by the relatively low splitting constant (0·2 mT) of the β-proton. By using the $\cos^2\theta$ relationship, the angle (θ) between the β-C–H bond and the π orbital of the α-carbon can be calculated to be *c.* 49°. Examination of a model shows that if the two vinylic protons were *cis*, the least hindered conformation would be attained for $\theta \approx 0°$, which would result in a larger value for a_β^{H}.

On freezing a toluene solution of (28) to a rigid glass, in the presence of silver oxide, the e.s.r. spectrum (Fig. 1) showed three weak pairs of lines symmetrically arranged about the central large signal. From the separation of these lines the zero-field splitting parameters[17] were found to be D 4·03 ± 0·5 mT and E 0·36 ± 0·02 mT, which gave an average interelectronic separation of 7·03 ± 0·02 Å. This is comparable to the separation of 6·32 Å found in bisgalvinoxyl.[10] Because of the weakness of the triplet signal we were unable to observe $\Delta m = \pm 2$ transitions. Recent studies of phenylgalvinoxyl (12; R = Ph)[18,19] indicate that it has a 'propeller' conformation with a twist angle of 30°. A similar angle of twist for the phenyl rings has been found

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[17] Wasserman, E., Snyder, L. C., and Yager, W. A., *J. Chem. Phys.*, 1964, **41**, 1763.
[18] Ishizu, K., Kamata, T., Mukai, K., and Tamaki, T., *Bull. Chem. Soc. Jpn*, 1976, **49**, 3376.
[19] Andersen, P., and Klewe, B., *Acta Chem. Scand.*, 1962, **16**, 1817.

for *p*- and *m*-phenylenebisgalvinoxyl biradicals.[20] Thus the 1,2-ethylenebisgalvinoxyl derived from (28) is also likely to be a weakly π-conjugated biradical with the low intensity of the $\Delta m = \pm 1$ absorptions being due to a weak electronic interaction.

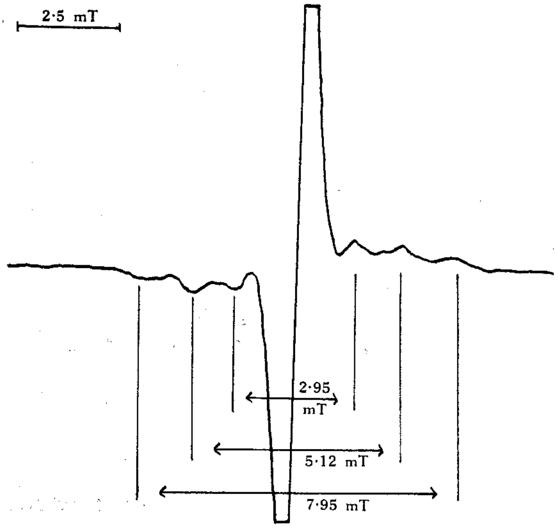
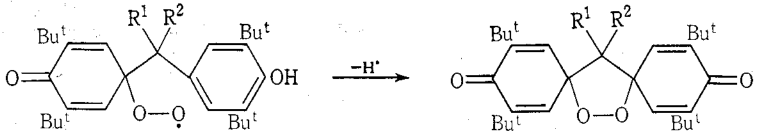


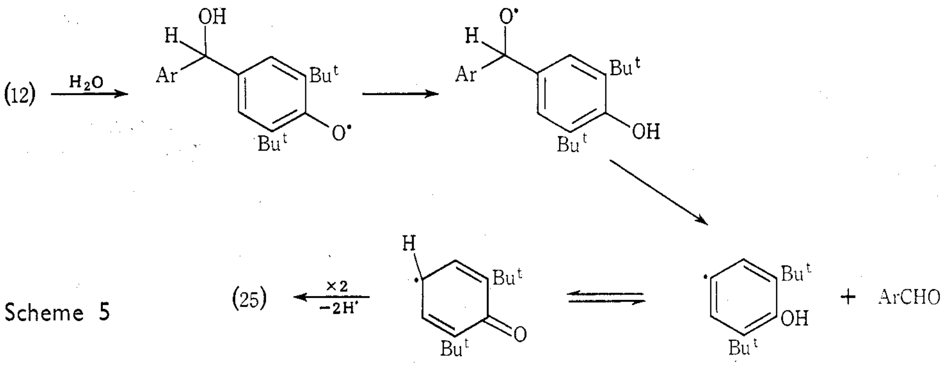
Fig. 1. E.s.r. spectrum at −100°C of the biradical derived from the bisquinonemethide (28).

Mechanistic Considerations

Formation of the spiroperoxides (16)–(22) seems more likely to involve reaction of the initial monophenoxy radicals with oxygen, followed by further oxidation, as in Scheme 4, rather than the direct addition of oxygen to a biradical. If the latter pathway were significant, biradicals should be observable in the absence of oxygen.



Scheme 4



Scheme 5

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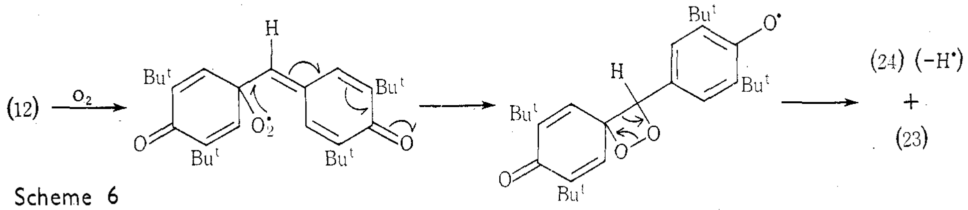
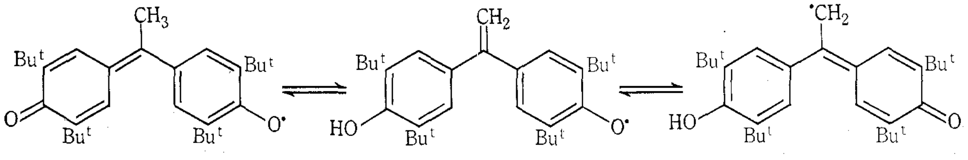
[20] Mukai, K., and Tamaki, T., *Bull. Chem. Soc. Jpn*, 1977, **50**, 1239.

The other compounds isolated in most of the oxidations were the quinones (23) and (25). Both may be produced in a variety of ways, all of which involve cleavage of the original diphenylmethane linkage. This may occur anaerobically, via a quinone-methide, as suggested by Müller *et al.*,[21] e.g. Scheme 5, or aerobically, as in Scheme 6.



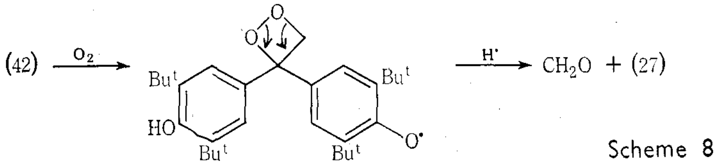
Scheme 6

A number of other pathways, including those which involve the extrusion of (25) from a coupled dimer, may be written. Schemes 5 and 6 are shown as examples only, and the quinones (23) and (25) have been isolated as the typical end products of the oxidation of 4-substituted 2,6-di-t-butylphenols on numerous occasions and with a variety of oxidants.[22] The formation of the bisquinonemethide (26) clearly involves coupling of two galvinoxyl radicals at the benzylic position.

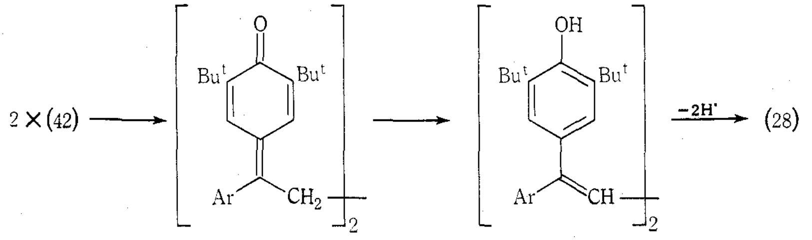


(13) (42)

Scheme 7



Scheme 8



(43)

Scheme 9

The remaining oxidation products are derived from the diphenylethane (2). In order to account for them it appears necessary to postulate a tautomeric equilibrium

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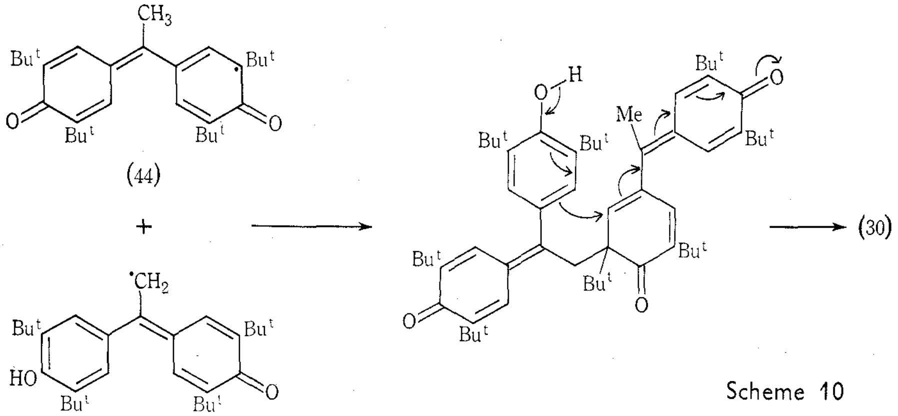
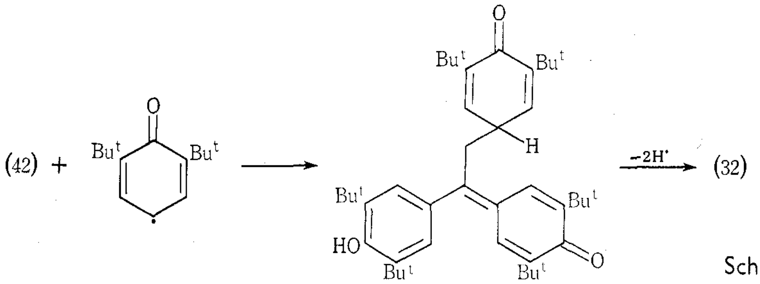
[21] Müller, E., Mayer, R., Heilmann, U., and Scheffler, K., *Justus Liebigs Ann. Chem.*, 1961, **645**, 66.
[22] Forrester, A. R., Hay, J. M., and Thomson, R. H., 'Organic Chemistry of Stable Free Radicals' Ch. 7 (Academic Press: London 1968).

between the galvinoxyl radical (13) and a methylene radical (42) as shown in Scheme 7. Thus the benzophenone (27) might be formed from (42) by loss of formaldehyde from a cyclic peroxide as in Scheme 8. Formation of the bisquinonemethide (28), surely a free radical process, provides much stronger evidence for the participation of radical (42). As in Scheme 9, dimerization of (42) would lead to the substituted ethane (43), and a further tautomeric shift, followed by oxidation, would give (28). In fact, after one oxidation of (2) with ferricyanide, in which the initial chromatographic separation of the products was performed rapidly, a small quantity (2 %) of a compound with spectroscopic properties compatible with those expected for the ethane (43) was isolated.



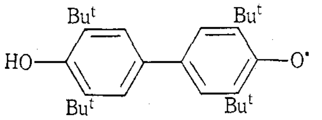
Scheme 10

Coupling of the radical (42) with a mesomeric form (44) of the galvinoxyl radical (13), as in Scheme 10, also provides a simple route to the indane derivative (30). Moreover, the formation of the quinonemethide (32) appears to involve the capture of a 2,6-di-t-butylphenoxy radical by radical (42), as in Scheme 11. The isolation of this compound thus provides some additional evidence for the formation of the 2,6-di-t-butylphenoxy radical in the oxidation of bisphenol (2). Although various fragmentations and couplings may be proposed to account for the formation of the stilbenequinone (31), in the absence of any evidence we hesitate to make a specific proposal.



Scheme 11

Much mention has been made of the radical (42). In an attempt to detect this, samples were withdrawn periodically from the silver oxide oxidation of the bisphenol (2), filtered, degassed, and examined by e.s.r. Initially, the only signal observed was that of the monophenoxy radical. The spectra then became more complex, but after 5 h the chief radical present was the galvinoxyl (13). After 1 week this had largely been replaced by a triplet, *a* 0·105 mT, with the same *g* value. The expected triplet-of-triplets spectrum of (42) was not observed, which indicates that, if the equilibrium of Scheme 7 operates, its position must be far to the left. The identity of the radical responsible for the 0·105 mT triplet spectrum has not been established, although it may be noted that the radical (45), which may well be a component of the oxidation mixture, exhibits a triplet splitting of similar size, 0·11 mT.[23]



(45)

Experimental

Melting points were taken with a Kofler hot-stage apparatus and are uncorrected. ^{1}H n.m.r. spectra, all of carbon tetrachloride solutions, were recorded with Varian A60 or Bruker HX-90 instruments. ^{13}C n.m.r. spectra were measured at the National N.M.R. Centre, Australian National University, Canberra. Low-resolution mass spectra were obtained with a Varian MAT CH-7 instrument, and high-resolution spectra with a Varian MAT 311 instrument, the latter at King Edward Memorial Hospital. Molecular weights were obtained by mass matching with the bisquinonemethide (28) ($M^{+\bullet}$ calc. 868·63696). E.s.r. spectra were recorded with a Varian V4500 instrument, and all spectra were successfully simulated by computer. H.f.s. constants were estimated to have an error of ±0·004 mT. Alumina for chromatography was neutral, activity I. Extracts were dried with anhydrous magnesium sulfate. Silver oxide was prepared by the method of Ohme and Schmitz.[24] Microanalyses were by the Australian Microanalytical Service, Melbourne.

Table 5. Physical constants of the bisphenols

Bis-phenol	Ref.	M.p. (°C)	Yield (%)	Molecular formula	Found (% or u)	Required (% or u)
(1)	4	154–155 (lit. 154)				
(2)	3	159·5–160·5	28	$C_{30}H_{46}O_2$	C, 82·2; H, 10·6	C, 82·2; H, 10·5
(3)	25	155–156	25	$C_{31}H_{48}O_2$	$M^{+\bullet}$ 452·3654	$M^{+\bullet}$ 452·3654
(4)	—	160–160·5	60	$C_{32}H_{50}O_2$	$M^{+\bullet}$ 466·3804	$M^{+\bullet}$ 466·3811
(6)	26	121–122	45	$C_{32}H_{50}O_2$	$M^{+\bullet}$ 466·3836	$M^{+\bullet}$ 466·3811
(7)	27	178–179	42	$C_{34}H_{52}O_2$	C, 83·0; H, 10·7	C, 82·9; H, 10·6

Preparation of the Bisphenols (2)–(7)

Most of these have been described in the patent literature.[25–27] For this work all were prepared by the base-catalysed (NaOH) condensation of the appropriate aldehyde or ketone with 2,6-di-t-butylphenol in refluxing methanol or ethanol over a period not less than 24 h under nitrogen. The bisphenols obtained on acidification were crystallized from ethanol or aqueous ethanol, and had n.m.r. spectra fully compatible with their structures. Physical constants are listed in Table 5.

In some instances unexpected results were obtained. Thus, a better yield (54%) of (2) was achieved when the condensation was carried out by refluxing the phenol with cyclohexanone in

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[23] Colegate, S. M., Hewgill, F. R., and Howie, G. B., *Aust. J. Chem.*, 1975, **28**, 343.
[24] Ohme, R., and Schmitz, E., *Org. Synth.*, 1973, Coll. Vol. V, 897.
[25] Br. Pat. 1,088,455 (*Chem. Abstr.*, 1968, **68**, 98647).
[26] U.S. Pat. 2,734,088 (*Chem. Abstr.*, 1956, **50**, 16855).
[27] U.S. Pat. 2,883,364 (*Chem. Abstr.*, 1959, **53**, 15621).

ethanol for 90 h. Reaction with cyclohexanone in methanol gave the cyclohexylidene compound (7). Similarly, attempted condensation of the phenol with butan-2-one in ethanol gave the ethylidene compound (2) (30%) rather than the 1-methylpropylidene compound (6), whereas with methanol as the solvent (6) was obtained. In the absence of solvent no reaction could be detected after 7 days of refluxing. With the long reaction times employed there is evidently an equilibrium between alcohol and ketone similar to that involved in Oppenauer oxidation, in which ethanol but not methanol can be oxidized. With the aldehydes propanal and 2-methylpropanal condensation occurred normally in ethanol without this complication.

Oxidation of Bisphenol (1)

(i) *By silver oxide.*—A solution of (1) in benzene (0·05 M) was shaken with silver oxide (1 equiv.) in oxygen for 8 h; approximately 1 equiv. of oxygen was absorbed. Evaporation of the filtered solution and crystallization of the residue gave *2,4,10,12-tetra-t-butyl-14,15-dioxadispiro[5,1,5,2]-pentadeca-1,4,9,12-tetraene-3,11-dione* (16) as pale yellow plates, m.p. 177–179° (72%) (Found: C, 76·5; H, 9·0. $C_{29}H_{42}O_4$ requires C, 76·7; H, 9·3%). N.m.r. δ 1·23, 36H, Bu^t; 2·63, 2H, CH_2; 6·60, 4H, olefinic. I.r. (CCl_4) 1670, 1645 and 1619 cm^{-1}. Mass spectrum 454 (M), 422 (28%, $M-O_2$).

(ii) *By ferricyanide.*—A solution of (1) in chloroform (0·05 M) was shaken with a solution of potassium ferricyanide (4 equiv., 0·25 M) and potassium hydroxide (2 equiv.) in water for 4 min. The chloroform layer was separated, dried and evaporated to afford a dark red oil. This was chromatographed on alumina. Elution with light petroleum/chloroform gave the following fractions:

(A) 2,6-Di-t-butyl-1,4-benzoquinone (23) (0–15%), m.p. and mixed m.p. 66·5–67·5° (lit.[28] 65–66).

(B) 3,3′,5,5′-Tetra-t-butyl-4,4′-diphenoquinone (25) (5–20%), m.p. and mixed m.p. 239·5–240° (lit.[29] 240–241).

(C) The spiroperoxide (16) (15–35%).

(D) 2,6-Di-t-butyl-4-(3,5-di-t-butyl-4-hydroxybenzylidene)cyclohexa-2,5-dienone (8) (0–25%), m.p. and mixed m.p. 158–159° (lit.[2] 157–158).

(E) 3,5-Di-t-butyl-4-hydroxybenzaldehyde (24) (0–10%), m.p. and mixed m.p. 187–188° (lit.[30] 189).

(F) 4,4′-[Bis(3,5-di-t-butyl-4-hydroxyphenyl)ethanediylidene]bis(2,6-di-t-butylcyclohexa-2,5-dien-1-one) (26) (5–15%), m.p. in an evacuated capillary 310–311° (lit.[10] 306–308) (Found: C, 82·4; H, 10·2. Calc. for $C_{58}H_{82}O_4$: C, 82·7; H, 9·7%). N.m.r. δ 1·12, 18H, 2 olefinic Bu^t; 1·28, 18H, 2 olefinic Bu^t; 1·37, 36H, 4 ArBu^t; 5·30, 2H, OH; 6·79, 2H, d, J 3 Hz, olefinic H; 6·98, 4H, ArH; and 7·36, 2H, d, J 3 Hz, olefinic H. Mass spectrum 842 (10%, M), 844 (100, M+2).

On hydrogenation in ethanol over palladium–charcoal the bisquinonemethide (26) absorbed 2 equiv. of hydrogen. The product, 4,4′,4″,4‴-ethanediylidenetetrakis(2,6-di-t-butylphenol), had m.p. 333–334° in an evacuated capillary (lit.[10] 330). N.m.r. δ 1·32, 72H, Bu^t; 4·27, 2H, methine H; 4·80, 4H, OH; and 6·93, 8H, ArH. Mass spectrum 846 (M).

Oxidation of Bisphenol (2)

(i) *By ferricyanide.*—A solution of the ethylidenebisphenol (2) (1 equiv.) in chloroform (0·1 M) was shaken with a solution of potassium ferricyanide (4 equiv.) and sodium hydroxide (2 equiv.) in water for 4 min. The chloroform layer was separated, dried and set aside in air for 2 h. Removal of the solvent under reduced pressure left an orange solid which was chromatographed on alumina and eluted with light petroleum/chloroform. The fractions so obtained were in some instances rechromatographed. Fractional recrystallization then afforded the following compounds:

(A) 3,3′,5,5′-Tetra-t-butyl-4,4′-diphenoquinone (25) (0–20%).

(B) 2,6-Di-t-butyl-1,4-benzoquinone (23) (5–10%).

(C) 3,3′,5,5′-Tetra-t-butyl-4,4′-dihydroxybenzophenone (27) (7–20%), m.p. and mixed m.p. 226–227° (lit.[23] 226·5–227).

(D) *2,4,10,12-Tetra-t-butyl-7-methyl-14,15-dioxadispiro[5,1,5,2]pentadeca-1,4,9,12-tetraene-3,11-dione* (17) (0–95%), needles, m.p. 139·5–140·5°, from aqueous ethanol (Found: C, 77·2; H, 9·5.

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[28] Metro, S. J., *J. Am. Chem. Soc.*, 1955, **77**, 2901.

[29] Mayer, R., Müller, E., Rieker, A., and Scheffler, K., *Justus Liebigs Ann. Chem.*, 1961, **645**, 36.

[30] Campbell, T. W., and Coppinger, G. M., *J. Am. Chem. Soc.*, 1953, **75**, 734.

$C_{30}H_{44}O_4$ requires C, 76·9; H, 9·4%). N.m.r. δ 0·52, 3H, d, J 7 Hz, Me; 1·25, 36H, Bu^t; 2·80, 1H, q, J 7 Hz, methine; 6·45, 2H, d, J 2·5 Hz, olefinic; 6·55, 2H, d, J 2·5 Hz, olefinic. I.r. (CCl_4) 1668, 1648, 1619 cm^{-1}. U.v. (cyclohexane) 252 nm (ε 22700). Mass spectrum 468 (M), 436 (M−32).

(E) *4,4′-[1,4-Bis(3,5-di-t-butyl-4-hydroxyphenyl)but-2-enediylidene]bis(2,6-di-t-butyl-2,5-cyclohexadien-1-one)* (28) (7–20%), solvated red crystals from n-pentane with a green metallic lustre, m.p. 288–289° (Found: C, 82·9; H, 9·8. $C_{60}H_{84}O_4$ requires C, 82·8; H, 9·7%). N.m.r. δ 1·10, 18H, olefinic Bu^t; 1·18, 18H, olefinic Bu^t; 1·52, 36H, $ArBu^t$; 5·33, 2H, OH; 6·70, 2H, d, J 2 Hz, olefinic H; 7·02, 4H, ArH; 7·15, 2H, d, J 2 Hz, olefinic H; 7·22, 2H, ethylenic H. U.v. (cyclohexane) 501·6 (ε 104800), 457·6 (77200), 440 (36800), 280 nm (14080). Mass spectrum 868 (M).

On hydrogenation of (28) in ethanol over palladium–charcoal 3 equiv. of hydrogen were absorbed. The product, *4,4′,4″,4‴-butanediylidenetetrakis(2,6-di-t-butylphenol)* (34) was obtained as needles, m.p. 244–245°, from aqueous ethanol (Found: $M^{+\cdot}$, 874·6839. $C_{60}H_{90}O_4$ requires $M^{+\cdot}$, 874·6839). N.m.r. δ 1·38, 72H, Bu^t; 1·87, 4H, d, J 6 Hz, CH_2; 3·67, 2H, t, J 6 Hz, methine; 4·83, 4H, OH; 6·87, 8H, ArH. I.r. (CCl_4) 3650 cm^{-1}.

(ii) *By silver oxide under oxygen.*—A solution of the bisphenol (2) in benzene (0·02 M) was shaken with silver oxide (2 equiv.) in oxygen. In 8 h 1 equiv. of oxygen was absorbed. Evaporation of the filtered solution left a yellow solid which on recrystallization from aqueous ethanol gave the spiro peroxide (17) (47%), m.p. and mixed m.p. 139·5–140·5°.

(iii) *By silver oxide under nitrogen.*—Similar oxidation of (2) was carried out under nitrogen for 5–24 h depending on the progress of the reaction. The filtered solution was then set aside under nitrogen for several hours. The residue obtained after evaporation was chromatographed on alumina and eluted with light petroleum/chloroform. Further chromatography and recrystallization afforded the following fractions in variable yield:

(A) The diphenoquinone (25).

(B) 2,6-Di-t-butyl-1,4-benzoquinone (23).

(C) The spiroperoxide (17).

(D) *2,6-Di-t-butyl-4-[1′-(3,5-di-t-butyl-4-hydroxyphenyl)ethylidene]cyclohexa-2,5-dien-1-one* (9), obtained as an orange powder, m.p. 172–173°, from light petroleum (Found: $M^{+\cdot}$, 436·3320. $C_{30}H_{44}O_2$ requires $M^{+\cdot}$, 436·3341). N.m.r. δ 1·19, 9H, olefinic Bu^t; 1·33, 9H, olefinic Bu^t; 1·47, 18H, $ArBu^t$; 2·52, 3H, Me; 5·35, 1H, OH; 7·03, 1H, d, J 2·5 Hz, olefinic H; 7·10, 2H, ArH; 7·42, 1H, J 2·5 Hz, olefinic H. U.v. (cyclohexane) 366 (ε 17500), 289 (6920), 266·2 nm (7730).

(E) *3,3a′,5,5′-Tetra-t-butyl-2′-(3,5-di-t-butyl-4-hydroxyphenyl)-7′-[1-(3,5-di-t-butyl-4-hydroxyphenyl)-ethylidene]-3a′,4′,7′,7a′-tetrahydrospiro[cyclohexa-2,5-diene-1,1′-[1H]indene]-4,4′-dione* (29), obtained as pale yellow plates, m.p. 246–247°, from ether/n-pentane (Found: C, 82·6; H, 9·8. $C_{60}H_{86}O_4$ requires C, 82·7; H, 9·9%). ^1H n.m.r. δ 1·07, 9H, aliphatic Bu^t; 1·10, 18H, olefinic Bu^t; 1·24, 9H, olefinic Bu^t; 1·36, 18H, $ArBu^t$; 1·42, 18H, $ArBu^t$; 2·03, 3H, Me; 4·08, 1H, methine H; 5·05, 1H, OH; 5·09, 1H, OH; 6·34, 1H, olefinic H; 6·36, 1H, d, J 2·4 Hz, olefinic H; 6·47, 1H, d, J 2·4 Hz, olefinic H; 6·69, 2H, ArH; 6·72, 1H, olefinic H; 6·97, 2H, ArH. ^{13}C n.m.r. ($CDCl_3$) δ 198·8, C=O; 185·5, C=O; 152·0, C–OH; 151·4, C–OH; 145·9, 145·5, 143·4, 143·4, d; 143·3, 141·4, d; 141·0, 140·4, d; 134·1, 133·9, 132·1, 130·8, d; 126·4, 125·4, 123·5, d; 121·5, d; 65·6, 59·4, 53·6, d; 37·0, 34·7, 34·5, 34·0, 33·9. U.v. (cyclohexane) 327 (ε 32080), 258 nm (16800). Mass spectrum 870 (M).

By fractional crystallization of the crude oxidation product from acetone *3,3a′,5,5′-tetra-t-butyl-2′-(3,5-di-t-butyl-4-oxocyclohexa-2,5-dienylidene)-7′-[1-(3,5-di-t-butyl-4-hydroxyphenyl)ethylidene]-2′,3′,3a′,4′,7′,7a′-hexahydrospiro[cyclohexa-2,5-diene-1,1′-[1H]indene]-4,4′-dione* (30) was obtained as bright yellow needles, m.p. 186·5–187·5° (dec.) (Found: $M^{+\cdot}$, 870·6522. $C_{60}H_{86}O_4$ requires $M^{+\cdot}$, 870·6526). ^1H n.m.r. δ 1·03, 9H, aliphatic Bu^t; 1·09, 18H, olefinic Bu^t; 1·13, 9H, olefinic Bu^t; 1·31, 9H, olefinic Bu^t; 1·34, 9H, olefinic Bu^t; 1·44, 18H, $ArBu^t$; 2·06, 3H, Me; 2·71, 1H, d, J 18·5 Hz, CH_2; 3·99, 1H, d, J 18·5 Hz, CH_2; 4·02, 1H, methine H; 5·13, 1H, OH; 6·20, 1H, d, J 2·5 Hz, olefinic H; 6·53, 1H, d, J 2·5 Hz, olefinic H; 6·70, 3H, 2ArH, 1 olefinic H; 6·80, 1H, olefinic H; 7·24, 1H, d, J 2 Hz, olefinic H. ^{13}C n.m.r. ($CDCl_3$) δ 199·3, C=O; 187·7, C=O; 186·9, C=O; 159·0, C=C; 153·4, C–OH, 147·4, C=C; 147·1, 145·6, 145·4, 144·6, 144·4, d; 142·2, 142·0, d; 140·6, d; 132·5, 129·6, d; 128·1, 127·8, d; 126·3, 61·1, 57·1, 55·6, d; 38·9, dd; 36·7, 35·2, 34·8, 34·4. U.v. (cyclohexane) 329·8 (ε 35100), 240·6 nm (ε 12900).

Hydrogenation of compounds (29) and (30) in ethanol over palladium–charcoal required 1 equiv. of hydrogen, and in both cases gave *3,3a′,5,5′-tetra-t-butyl-2′-(3,5-di-t-butyl-4-hydroxyphenyl)-*

7′-[1-(3,5-di-t-butyl-4-hydroxyphenyl)ethylidene]-2′,3′,3a′,4′,7′,7a′-hexahydrospiro[cyclohexa-2,5-diene-1,1′-[1H]indene]-4,4′-dione (35) as needles, m.p. 154–155° (dec.), from aqueous ethanol (Found: M$^{+\cdot}$, 872·6683. $C_{60}H_{88}O_4$ requires M$^{+\cdot}$, 872·6648). ^{1}H n.m.r. δ 0·89, 9H, aliphatic Bu^t; 1·06, 9H, olefinic Bu^t; 1·08, 9H, olefinic Bu^t; 1·23, 9H, olefinic Bu^t; 1·37, 36H, ArBu^t; 2·10, 3H, Me; 3·14, 3H, m, CH and CH_2; 3·87, 1H, methine H; 4·87, 1H, OH; 5·04, 1H, OH; 6·08, 1H, d, J 2·5 Hz, olefinic H, 6·50, 1H, d, J 2·5 Hz, olefinic H; 6·59, 3H, 2ArH, 1 olefinic H; 6·82, 2H, ArH. U.v. (cyclohexane) 319·6 (ε 10000), 283 (9500), 233 nm (17500).

A solution of (29) in dry tetrahydrofuran was added to a stirred suspension of sodium hydride in dry tetrahydrofuran under nitrogen. Methyl iodide (3 equiv.) was then added and the mixture was stirred under reflux for 24 h while the purple colour of the phenolate anion faded. When the mixture had cooled, the excess of sodium hydride was destroyed by ethanol; the solution was poured into water and extracted with ether. Evaporation of the dried extract gave *3,3a′,5,5′-tetra-t-butyl-2′-(3,5-di-t-butyl-4-methoxyphenyl)-7′-[1-(3,5-di-t-butyl-4-methoxyphenyl)ethylidene]-3a′,4′,7′,7a′-tetrahydrospiro[cyclohexa-2,5-diene-1,1′-[1H]indene]-4,4′-dione* as a pale yellow powder, m.p. 233–234° (dec.), from aqueous ethanol (Found: M$^{+\cdot}$, 898·6857. $C_{62}H_{90}O_4$ requires M$^{+\cdot}$, 898·6839). N.m.r. δ 1·09, 9H, aliphatic Bu^t; 1·11, 9H, olefinic Bu^t; 1·13, 9H, olefinic Bu^t; 1·25, 9H, olefinic Bu^t; 1·35, 18H, ArBu^t; 1·40, 18H, ArBu^t; 2·07, 3H, Me; 3·63, 3H, OMe; 3·66, 3H, OMe; 4·14, 1H, broad, methine; 6·44, 1H, d, J 2·5 Hz, olefinic H; 6·52, 1H, olefinic H; 6·58, 1H, d, J 2·5 Hz, olefinic H; 6·71, 1H, broad, olefinic H; 6·83, 2H, ArH; 7·12, 2H, ArH.

(iv) *By manganese dioxide*.—A solution of the bisphenol (2) in benzene (0·02 M) was added to a stirred suspension of manganese dioxide (2 equiv.) in benzene under nitrogen. After 3 h the filtered solution was evaporated. Crystallization of the residue from n-pentane gave an orange powder, m.p. 163–165°, tentatively identified as a charge transfer complex between (2) and (9). N.m.r. δ 1·20, 9H, olefinic Bu^t; 1·33, 9H, olefinic Bu^t; 1·40, 36H, ArBu^t; 1·47, 18H, ArBu^t; 1·60, 3H, d, J 7 Hz, Me; 2·52, 3H, Me; 3·80, 1H, q, J 7 Hz, methine; 4·87, 2H, OH; 5·30, 1H, OH; 6·92, 2H, ArH; 7·03, 1H, d, J 2 Hz, olefinic H; 7·10, 4H, ArH; 7·42, 1H, d, J 2 Hz, olefinic H. Mass spectrum 438·436 (M$^{+\cdot}$).

(v) *By lead dioxide*.—A solution of the bisphenol (2) in benzene was stirred under reflux with an excess of lead dioxide under nitrogen. After 3 days the mixture was filtered and the solvent was evaporated to leave a red gum. This was adsorbed on alumina and eluted with light petroleum/chloroform. Crystallization of the fractions afforded some of the bisphenol (2) and the following oxidation products:

(A) 2,6-Di-t-butyl-1,4-benzoquinone (23) (10–20%).

(B) 3,3′,5,5′-Tetra-t-butylstilbene-4,4′-quinone (31) (0–15%).

This was obtained only from more vigorous oxidation of concentrated solutions. It had m.p. 303–304° (lit.[31] 296–301), from aqueous ethanol. The m.p. was not depressed on admixture with a sample prepared by the method of Cook.[31]

(C) The quinonemethide (31) (0–10%).

(D) *4,4′-[1″-(3,5-Di-t-butyl-4-hydroxyphenyl)ethanediylidene]bis(2,6-di-t-butylcyclohexa-2,5-dien-1-one)* (32) (5–25%), which crystallized from aqueous ethanol as crimson needles, m.p. 256–257° (Found: M$^{+\cdot}$, 638·4626. $C_{44}H_{62}O_3$ requires M$^{+\cdot}$, 638·4699). N.m.r. δ 0·94, 9H, olefinic Bu^t; 1·19, 9H, olefinic Bu^t; 1·33, 18H, olefinic Bu^t; 1·45, 18H, ArBu^t; 5·40, 1H, OH; 6·47, 1H, d, J 2·2 Hz, olefinic H; 6·72, 2H, olefinic H; 7·04, 2H, ArH; 7·29, 1H, olefinic H; 7·35, 1H, d, J 2·4 Hz, olefinic H.

Hydrogenation of (32) in ethanol over palladium–charcoal required 2 equiv. of hydrogen. The product was crystallized from aqueous ethanol, giving *2-(3,5-di-t-butyl-4-hydroxyphenyl)ethylidenebis(2,6-di-t-butylphenol)* (36) as needles, m.p. 186–187° (Found: M$^{+\cdot}$, 642·4959. $C_{44}H_{66}O_3$ requires 642·5012). N.m.r. δ 1·30, 18H, Bu^t; 1·40, 36H, Bu^t; 3·10, 2H, d, J 6 Hz, CH_2; 3·83, 1H, t, J 6 Hz, methine; 4·75, 1H, OH; 4·82, 2H, OH, 6·60, 2H, ArH; 6·92, 4H, ArH.

Oxidation of Bisphenol (3)

(i) *By ferricyanide*.—A solution of the propylidenebisphenol (3) (1 equiv.) in chloroform (0·06 M) was added to a stirred solution of potassium ferricyanide (4 equiv.) and potassium hydroxide (2 equiv.) in water under nitrogen. In separate experiments the reaction time was varied from 1 to 24 h but the product composition did not change. The chloroform layer was separated, dried and

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[31] Cook, C. D., *J. Org. Chem.*, 1953, **18**, 261.

evaporated, and the residue was chromatographed on alumina with light petroleum/chloroform, giving the following products:

(A) 2,6-Di-t-butyl-1,4-benzoquinone (23) (8%).

(B) 3,3′,5,5′-Tetra-t-butyl-4,4′-diphenoquinone (25) (5%).

(C) *2,4,10,12-Tetra-t-butyl-7-ethyl-14,15-dioxadispiro[5,1,5,2]pentadeca-1,4,9,12-tetraene-3,11-dione* (18), which was obtained in higher yield (up to 60%) when the oxidation time was shorter and when the solution was exposed to air. Recrystallization from aqueous ethanol gave needles, m.p. 146·5–147·5° (Found: C, 77·4; H, 9·4. $C_{31}H_{46}O_4$ requires C, 77·2; H, 9·5%). N.m.r. δ 0·94, 3H, m, Me; 1·20, 2H, m, CH_2; 1·24, 18H, Bu^t; 1·26, 18H, Bu^t; 2·57, 1H, t, *J* 7·5 Hz, methine H; 6·47, 2H, d, *J* 3 Hz, olefinic H; 6·61, 2H, d, *J* 3 Hz, olefinic H. I.r. (CCl_4) 1668, 1648, 1619 cm^{-1}. Mass spectrum 482 (M), 450 (M − 32).

(D) *2,6-Di-t-butyl-4-[1-(3,5-di-t-butyl-4-hydroxyphenyl)propylidene]cyclohexa-2,5-dien-1-one* (10), which was formed in highest yield (30%) when the radicals were allowed to decay for several days under nitrogen. Recrystallization from aqueous ethanol gave bright yellow needles, m.p. 168–169° (Found: C, 82·6; H, 10·5. $C_{31}H_{46}O_2$ requires C, 82·7; H, 10·2%). N.m.r. δ 1·14, 3H, t, *J* 7·5 Hz, Me; 1·17, 9H, olefinic Bu^t; 1·33, 9H, olefinic Bu^t; 1·48, 18H, $ArBu^t$; 2·87, 2H, q, *J* 7·5 Hz, CH_2; 5·28, 1H, OH; 6·90, 1H, d, *J* 2·5 Hz, olefinic H; 7·04, 2H, ArH; 7·35, 1H, d, *J* 2·5 Hz, olefinic H. U.v. (cyclohexane) 363·4 (ε 23550), 294·6 (7650), 265·6 (7200), 248·2 nm (infl.). Mass spectrum 450 (M), 393 (M − 57).

(ii) *By silver oxide*.—A solution of bisphenol (3) in benzene (0·03 M) was stirred with silver oxide (2 equiv.) under nitrogen. The residue obtained after filtration and evaporation of the solvent was chromatographed on alumina with light petroleum, giving:

(A) 2,6-Di-t-butyl-1,4-benzoquinone (23) (2–10%).

(B) 3,3′,5,5′-Tetra-t-butyl-4,4′-diphenoquinone (25) (5–20%).

(C) The cyclohexadienone (10) (5–30%).

(D) The spiroperoxide (18) (8–60%).

The yields of (B) and (C) were increased by longer reaction times, while the yield of the spiroperoxide (D) was increased by an oxygen atmosphere, and shorter reaction time.

Oxidation of Bisphenol (4)

(i) *By ferricyanide*.—A solution of the isobutylidenebisphenol (4) in chloroform (0·08 M) was added to a stirred solution of potassium ferricyanide (4 equiv.) and potassium hydroxide in water, under nitrogen. After stirring for 10–24 h the chloroform layer was separated, dried and evaporated, leaving a dark red solid. This was recrystallized from light petroleum to give red needles, m.p. 97–98° (up to 60%), tentatively formulated as (39). The mother liquor was evaporated and the residue was chromatographed on alumina with light petroleum/chloroform giving:

(A) 2,6-Di-t-butyl-1,4-benzoquinone (23) (0–6%).

(B) 3,3′,5,5′-Tetra-t-butyl-4,4′-diphenoquinone (25) (0–8%).

(C) *2,4,10,12-Tetra-t-butyl-7-isopropyl-14,15-dioxadispiro[5,1,5,2]pentadeca-1,4,9,12-tetraene-3,11-dione* (19), the yield of which increased with increasing exposure of the red solution to air, with a corresponding decrease in the amount of the red solid that crystallized. Recrystallization of (19) from n-pentane gave the spiroperoxide as *needles*, m.p. 167–169° (Found: C, 77·7; H, 9·7. $C_{32}H_{48}O_4$ requires C, 77·4; H, 9·7%). N.m.r. δ 0·64, 6H, d, *J* 6·2 Hz, Me; 1·24, 18H, Bu^t; 1·28, 18H, Bu^t; 1·71, 1H, m, methine H; 2·41, 1H, d, *J* 11·4 Hz, methine H; 6·42, 2H, d, *J* 3 Hz, olefinic H; 6·74, 2H, d, *J* 3 Hz, olefinic H. U.v. (cyclohexane) 254 (ε 19000), 212·2sh nm. I.r. (CCl_4) 1666, 1648, 1620 cm^{-1}. Mass spectrum 496 (M), 464 (M − 32).

(ii) *By silver oxide*.—A solution of (4) in benzene (0·08 M) was stirred with silver oxide (2 equiv.) under nitrogen for 5 h. The filtered reaction mixture was set aside under nitrogen for several hours until the free radicals had decayed. Evaporation of the solvent and crystallization of the residue from light petroleum gave the red solid (39) (20–45%). The mother liquor was chromatographed as before, giving:

(A) 2,6-Di-t-butyl-1,4-benzoquinone (23) (0–10%).

(B) 3,3′,5,5′-Tetra-t-butyl-4,4′-diphenoquinone (25) (5–15%).

(C) 3,3′,5,5′-Tetra-t-butyl-4,4′-dihydroxybenzophenone (27) (0–12%).

(D) The spiroperoxide (19) (20–40%).

(E) *2,6-Di-t-butyl-4-[1-(3,5-di-t-butyl-4-hydroxyphenyl)-2-methylpropylidene]cyclohexa-2,5-dien-1-one* (11) (2–5%), which was separated from the spiroperoxide (19) by fractional crystallization from n-pentane; bright yellow needles, m.p. 152–153° (Found: $M^{+\cdot}$, 464·3654. $C_{32}H_{48}O_2$ requires $M^{+\cdot}$, 464·3654). N.m.r. δ 1·08, 9H, olefinic Bu^t; 1·25, 6H, d, J 6 Hz, Me; 1·33, 9H, olefinic Bu^t; 1·45, 18H, ArBu^t; 3·58, 1H, septet, J 6 Hz, methine; 5·20, 1H, OH; 6·56, 1H, d, J 3 Hz, olefinic H; 6·85, 2H, ArH; 7·47, 1H, d, J 3 Hz, olefinic H.

Reactions of the Red Complex (*39*)

Hydrogenation of compound (39) in ethanol over palladium–charcoal required 1 equiv. of hydrogen and gave only the butylidenebisphenol (4), m.p. and mixed m.p. 160–161°.

Red solutions of (39) in light petroleum, benzene or ethanol faded to pale orange after exposure to air for 24 h. Evaporation, and recrystallization of the residues from n-pentane, gave almost quantitative yields of the spiroperoxide (19).

A solution of (39) in acetic acid almost immediately faded to a yellow colour. It was poured into water and extracted with ether. After washing with sodium bicarbonate and water, the dried extract was evaporated. This left a yellow oil, which was adsorbed on alumina and eluted with light petroleum to give 2,6-di-t-butyl-1,4-benzoquinone (23) (20–40%), and 1-(3,5-di-t-butyl-4-hydroxyphenyl)-2-methylpropanol (38) as prisms, m.p. 94–95°, from light petroleum (lit.[32] m.p. 83–87) (Found: C, 77·7; H, 10·8. Calc. for $C_{18}H_{30}O_2$: C, 77·7; H, 10·8%). N.m.r. δ 0·66, 3H, d, J 6·5 Hz, Me; 0·86, 3H, d, J 6·5 Hz, Me; 1·35, 18H, Bu^t; 1·51, 1H, OH; 1·75, 1H, m, methine H; 4·05, 1H, d, J 7·5 Hz, methine H; 4·96, 1H, ArOH; 6·91, 2H, ArH. Mass spectrum 278 (M). In view of the discrepancy in melting points an authentic sample was prepared as follows.

A solution of 2,6-di-t-butylphenol (14·5 g) in dry methylene chloride (50 ml) was added dropwise over 40 min to a stirred solution of 2-methylpropionyl chloride (7·4 g) and stannic chloride (18·2 g) in dry methylene chloride (30 ml). After 1 h the mixture was poured into dilute hydrochloric acid, and the organic layer was washed with water and dried. Evaporation of the solvent and crystallization of the residue from ethanol gave 1-(3,5-di-t-butyl-4-hydroxyphenyl)-2-methylpropan-1-one (45%), m.p. 139–140° (lit.[33] 125–127). N.m.r. 1·16, 6H, d, J 6·6 Hz, Me; 1·47, 18H, Bu^t; 3·45, 1H, septet, J 6·6 Hz, methine H; 5·66, 1H, OH; 7·69, 2H, ArH. Mass spectrum 276 (M).

Sodium borohydride (0·6 g) was added in portions to a solution of this phenol (1·3 g) in methanol. The mixture was stirred for 7 h, diluted with ethanol, then water, and the product was extracted with ether. Evaporation of the dried extract and crystallization of the residue from light petroleum gave the propanol (38) (70%) as prisms, m.p. and mixed m.p. 94–95°.

Oxidation of Bisphenol (*6*)

A solution of the bisphenol (6) in benzene (0·05 M) was stirred with silver oxide (2 equiv.) under nitrogen for 24 h. Filtration afforded a red solution which was divided into three portions.

The first portion was treated with hydroquinone, which led to the loss of the red colour. Evaporation, and crystallization of the residue from aqueous ethanol, gave the bisphenol (6).

The second portion was exposed to air until its colour had faded. Evaporation of the solvent and crystallization of the residue from aqueous ethanol gave *2,4,10,12-tetra-t-butyl-7-ethyl-7-methyl-14,15-dioxadispiro[5,1,5,2]pentadeca-1,4,9,12-tetraene-3,11-dione* (21) as needles, m.p. 113–114° (Found: C, 77·5; H, 10·0. $C_{32}H_{48}O_4$ requires C, 77·4; H, 9·7%). N.m.r. δ 0·58, 3H, t, J 7 Hz, Me; 1·15, 3H, Me; 1·25, 18H, Bu^t; 1·27, 18H, Bu^t; 6·56, 2H, d, J 3 Hz, olefinic H; 6·80, 2H, d, J 3 Hz, olefinic H; and *c.* 1·22, CH_2 (only the two high-field components of the quartet, J 7 Hz, were visible). I.r. (CCl_4) 1667, 1647, 1620 cm^{-1}. Mass spectrum: M was not observed; the compound cleaves to *m*/*e* 276 and 220.

The third portion was immediately evaporated to afford a red gum. Chromatography on alumina gave 2,6-di-t-butyl-1,4-benzoquinone (23) (14%), and the spiroperoxide (21) (55%).

Oxidation of Bisphenol (*7*)

(i) *By silver oxide under oxygen.*—A solution of the cyclohexylidenebisphenol (7) in benzene (0·05 M) was shaken with silver oxide (2 equiv.) under oxygen for 6 h. The initial colour faded to

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[32] Ershov, V. V., Portnykh, N. V., and Volod'kin, A. A., *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1968, 220 (*Chem. Abstr.*, 1968, **69**, 76799).

[33] Ershov, V. V., Portnykh, N. V., and Volod'kin, A. A., *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1966, 2243 (*Chem. Abstr.*, 1967, **66**, 85580).

pale yellow. Evaporation of the filtered solution and crystallization of the residue from ethanol gave *2,4,15,17-tetra-t-butyl-19,20-dioxatrispiro[5,0,5,0,5,2]eicosa-1,4,14,17-tetraene-3,16-dione* (22) (90%) as pale yellow plates, m.p. 107–109° (Found: C, 78·2; H, 9·9. $C_{34}H_{50}O_4$ requires C, 78·2; H, 9·6%). N.m.r. δ 1·27, 36H, Bu^t; *c.* 1·35, 10H, m, cyclohexyl H; 6·60, 4H, olefinic H. I.r. (CCl_4) 1668, 1648, 1620 cm^{-1}. Mass spectrum: M was not observed; the compound fragments to *m/e* 302 and 220.

(ii) *By silver oxide under nitrogen.*—Similar treatment under nitrogen gave, after filtration and evaporation, a red solid residue which was chromatographed on alumina. This gave the bisphenol (7) (30%), 2,6-di-t-butyl-1,4-benzoquinone (23) (40%) and the spiroperoxide (22) (10%).

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