# Phenol Oxidation Mechanisms.   A Search for Phenoxylium Intermediates

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Results which point to the occurrence of an ionic intramolecular coupling process in the oxidation of certain diphenyl ether and diphenylmethane derivatives are described.   This process is in contrast to the usual free-radical coupling route encountered under different conditions.   An attempt to induce a related heterolytic intramolecular coupling during the oxidation of some bis-hydroxynaphthylmethane monoethers was unsuccessful.

PARTICIPATION of phenoxyl radicals in the oxidation of phenols is now established.[1]   Moreover, the disappearance of these radicals by second-order processes clearly indicates the occurrence of coupling reactions.[2]   Despite this several authors have suggested other possibilities. One such, alluded to by both Barton[3] and Musso,[4] involves the reaction of a phenol with a phenoxylium cation, *viz.*

$$ \text{ArOH} + \text{ArO}^+ \longrightarrow \text{dimer} + \text{H}^+ $$
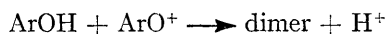
This process satisfies all the structural requirements of phenol oxidations.   Its occurrence is supported by the observations that two electrons may be removed electrochemically from a phenol, and that the removal of an electron from a phenoxyl radical is kinetically feasible under simple oxidation conditions.[5]   Moreover, the isolation of crystalline phenoxylium ion salts of strong acids [*e.g.* (1) as the hexachloroantimonate or the tetrafluoroborate] has been described;[6]   subsequently reactions involving electrophilic substitution by a phen-

oxylium cation into an anisole nucleus during the oxidation of certain benzophenones were reported.[7]

Oxidation of the bishydroxynaphthylmethane (2) gives the spironaphthalenone (3) in nearly quantitative yield.[8]   The derived monoethers (4)—(6) might thus have a considerable tendency to form structure (3), either through the radical (7) with extrusion of R·, or through the naphthyloxylium cation (8) with extrusion of R$^+$, as indicated (Scheme 1).   Methyl, benzyl, and *p*-nitrobenzyl ethers were studied to provide a range of stabilities for the extruded fragments and thus to permit further mechanistic deductions.   In the presence of suitable additives the radical R· would appear finally as RH, and the ion R$^+$ as ROH or its equivalent, after capture by a nucleophile.

The results of a series of oxidation experiments are summarised in Table 1.   No ordinary[9] oxidant was found to effect the desired change.   Reagents such as manganese dioxide, sodium bismuthate, and alkaline potassium ferricyanide, commonly used to produce phenoxyl radicals,[4] all gave excellent yields of the coupled products (9)—(11) from the respective naph-

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[1] E. Müller, K. Ley, G. Scheffler, and R. Mayer, *Chem. Ber.,* 1958, **91**, 2682, and subsequent papers; J. K. Becconsall, S. Clough, and G. Scott, *Proc. Chem. Soc.,* 1959, 308; *Trans. Faraday Soc.,* 1960, **56**, 459; T. J. Stone and W. A. Waters, *J. Chem. Soc.,* 1964, 213, 4302; F. R. Hewgill, T. J. Stone, and W. A. Waters, *ibid.,* p. 408; R. W. Kreilick, *J. Amer. Chem. Soc.,* 1966, **88**, 5284; B. T. Allen and A. Bond, *J. Phys. Chem.,* 1964, **68**, 2439.

[2] E. F. Zwicker and L. I. Grossweiner, *J. Chem. Phys.,* 1961, **34**, 1417; *J. Phys. Chem.,* 1963, **67**, 549; G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.,* 1965, **61**, 708; E. J. Land, G. Porter, and E. Strachan, *ibid.,* 1961, **57**, 1885; E. J. Land and G. Porter, *ibid.,* 1963, **59**, 2016; M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.,* 1967, **32**, 1.

[3] D. H. R. Barton, *Chem. in Britain,* 1967, **3**, 330.

[4] H. Musso in ' Oxidative Coupling of Phenols,' ed. W. I. Taylor and A. R. Battersby, Marcel Dekker, New York, 1967.

[5] F. J. Vermillian, jun. and I. A. Pearl, *J. Electrochem. Soc.,* 1964, **111**, 1392; C. A. Chambers and J. Q. Chambers, *J. Amer. Chem. Soc.,* 1966, **88**, 2922; R. Cecil and J. S. Littler, *J. Chem. Soc. (B),* 1968, 1420.

[6] K. Dimroth, W. Umbach, and H. Thomas, *Chem. Ber.,* 1967, **100**, 132.

[7] J. W. A. Findlay, P. Gupta, and J. R. Lewis, *Chem. Comm.,* 1969, 206.

[8] R. Pummerer and E. Cherbuliez, *Ber.,* 1914, **47**, 2957.

[9] R. G. R. Bacon and A. R. Izzat, *J. Chem. Soc. (C),* 1966, 791.

thols. Cerium(IV) ammonium sulphate (under neutral conditions), tetraethyl ammonium periodate, and chromium trioxide (in pyridine), which were expected to oxidise

(1) R = 4-MeO·C$_6$H$_4$

(2) R = H
(4) R = Me
(5) R = PhCH$_2$
(6) R = 4-O$_2$N·C$_6$H$_4$·CH$_2$

R = H

R ≠ H

(3)

(9) R = Me
(10) R = PhCH$_2$
(11) R = 4-O$_2$N·C$_6$H$_4$·CH$_2$

via a two-electron (*i.e.* ionic) reaction path, produced the same dimeric products.

Thallium(III) salts are reported [10] to be reduced by simultaneous addition of two electrons to give the

(3) + R· ⟶ RH

(7)

(3) + R$^+$ ⟶ ROH

(8)
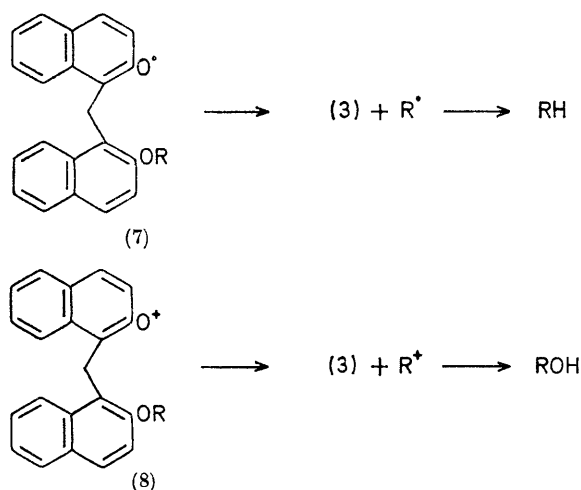
SCHEME 1

corresponding thallium(I) compounds. Subsequent work [11] has cast doubt on these conclusions, but if they were valid exposure of the naphthols to thallium(III) acetate could produce the cation (8) or an equivalent
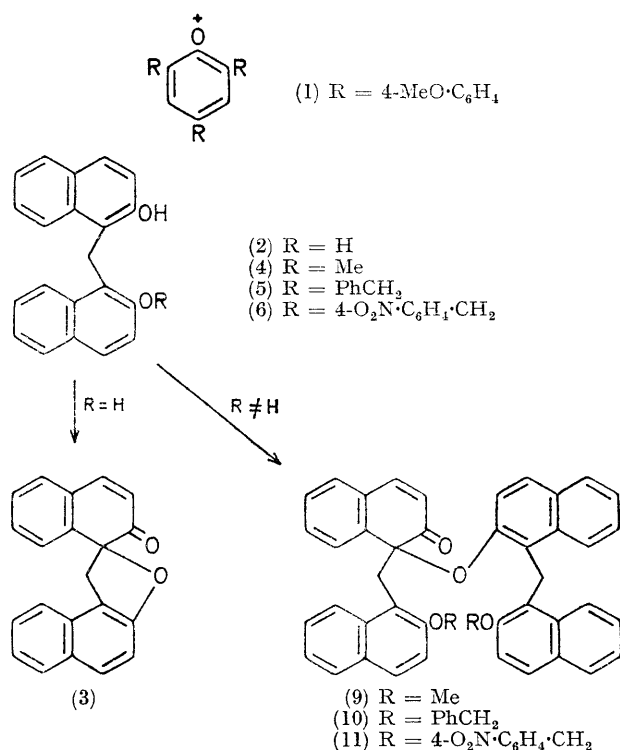
species. The reagent oxidised the monobenzyl ether (5) to the dimer (10) and the acetoxynaphthalenone (12). The latter product was formed in nearly quantitative yield by the action of lead tetra-acetate on the

TABLE 1

Oxidation of naphthol derivatives

Substrate	Oxidant	Product	Yield (%)
(2)	NaBiO$_3$–PhH	(3)	95
	Ce^{IV}–H$^+$	Intractable	
(4)	Fe(CN)$_6$$^{3-}$–OH$^-$	(9)	90
	Ce^{IV}–H$_2$O	No oxidation	
	MnO$_2$–PhH	(9)	100
	Et$_4$N$^+$IO$_4$$^-$–MeOH	(9)	30 (90) *
	Pb(OAc)$_4$	(13)	95
(5)	Fe(CN)$_6$$^{3-}$–OH$^-$	(10)	90
	NaBiO$_3$–PhH	(10)	90
	MnO$_2$–PhH	(10)	100
	Et$_4$N$^+$IO$_4$$^-$–MeOH	(10)	30
	Ce^{IV}–H$_2$O	(10)	85
	CrO$_3$–C$_5$H$_5$N	(10)	90
	HNO$_2$	(10)	75
	Tl(OAc)$_3$	(10)	20
		(12)	40
	Pb(OAc)$_4$	(12)	96
(6)	Fe(CN)$_6$$^{3-}$–OH$^-$	(11)	90
	MnO$_2$–PhH	(11)	95
	Et$_4$N$^+$IO$_4$$^-$–MeOH	(11)	45

* Based on oxidised naphthol.

naphthol (5), and a corresponding product (13) was likewise derived from the monomethyl ether (4). The absence of any dimeric products and of the naphthalenone (3) excludes radical and cationic intermediates, respectively. Formation of ketones (12) and (13) is

(14)

(12) R = PhCH$_2$
(13) R = Me
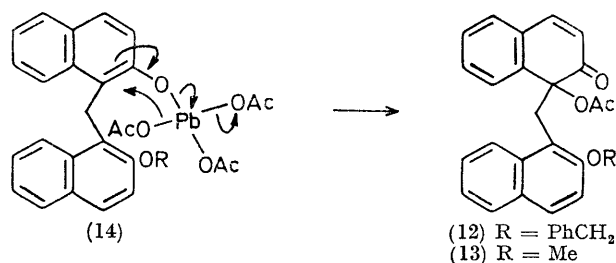
probably best rationalised as involving the formation and rearrangement of an organolead intermediate (14) or the corresponding thallium compound. In the latter case two processes (one-electron removal and complex formation) may compete. Alternatively, a complex may form and then react either by homolytic cleavage of the naphthol–thallium bond, or by intramolecular rearrangement.

Acidic reaction conditions, more likely to permit phenoxylium ion formation,[6,12] could not be explored because of the marked instability of the oxidation products in the presence of acid.
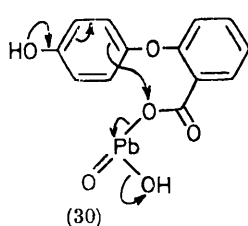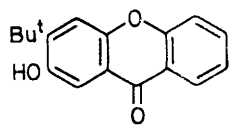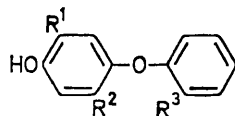
Failure to detect any cationic intermediates in the naphthol oxidations led to a study of the oxidation of some substituted diphenyl ethers, of which the acid (15) may be considered the parent. Hassall and Lewis[13]

[10] H. N. Halvorson and J. Halpern, *J. Amer. Chem. Soc.*, 1956, **78**, 5562; A. G. Sykes, *J. Chem. Soc.*, 1961, 5549; J. W. Gryder and M. C. Dorfman, *J. Amer. Chem. Soc.*, 1961, **83**, 1254.

[11] B. P. Sinha, *Z. phys. Chem.*, 1966, **233**, 161.
[12] F. R. Hewgill, B. R. Kennedy, and D. Kilpin, *J. Chem. Soc.*, 1965, 2904.
[13] C. H. Hassall and J. R. Lewis, *J. Chem. Soc.*, 1961, 2312.

found that this hydroxy-acid could be oxidatively cyclised by lead dioxide, forming the spiro-dienone (16) in 35% yield. Potassium ferricyanide did not effect this conversion. The absence of decarboxylated products, expected in the light of the postulation [14] of carboxyl radical intermediates,[15] argues against a free-radical mechanism. More significantly, for cross-coupling reactions (of which this may be considered an intramolecular example) to occur, it is necessary that both radical species (here phenoxyl and carboxyl) should be formed at similar rates.[16] This is unlikely to occur under the usual conditions of oxidation. The key intermediate could be the phenoxylium ion (18), which cyclises as indicated.

(17)

(16) R¹ = R² = H
(28) R¹ = Bu^t, R² = H
(29) R¹ = R² = Bu^t

(18)

(15) R¹ = R² = H, R³ = CO$_2$H
(19) R¹ = R² = H, R³ = CO$_2$Et
(20) R¹ = R² = H, R³ = CH$_2$·OH
(21) R¹ = Bu^t, R² = H, R³ = CO$_2$H
(22) R¹ = Bu^t, R² = H, R³ = CO$_2$Et
(23) R¹ = Bu^t, R² = H, R³ = CH$_2$·OH
(24) R¹ = R² = Bu^t, R³ = CO$_2$H
(25) R¹ = R² = Bu^t, R³ = CO$_2$Et
(26) R¹ = R² = Bu^t, R³ = CH$_2$·OH

(27)

(30)
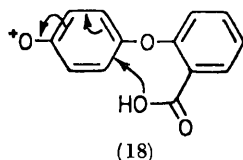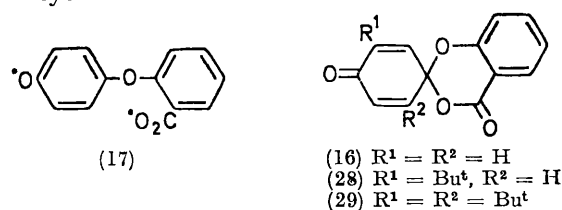
If this were the case, the ethyl ester (19) might also produce the spiro-compound (16) by the loss of ethyl cation or its equivalent, and the benzyl alcohol (20) could give a related dienone. To improve yields, by decreasing the potential for intermolecular coupling, and to increase the ease of oxidation the t-butylated compounds (21)—

(26) were used. These were all prepared by unexceptional means from the ethyl ester (19). An attempt to alkylate the hydroxy-acid (15) directly caused dehydration to the xanthone (27).

Table 2 is a summary of some of the oxidation reactions of these compounds. Two modes of reaction

TABLE 2
Oxidation of diphenyl ether derivatives

Substrate	Reagent	Product	Yield (%)
(15)	PbO$_2$	(16)	35 (ref. 13)
(19)	PbO$_2$–Et$_2$O	Intractable	
(20)	PbO$_2$–Et$_2$O	Intractable	
(21)	PbO$_2$–Et$_2$O	(28)	40
	Pb(OAc)$_4$–PhH	(28)	50
(22)	PbO$_2$–Et$_2$O	(33)	100
	Fe(CN)$_6$³⁻–OH⁻	(33)	100
(23)	PbO$_2$–Et$_2$O	Intractable	
	Fe(CN)$_6$³⁻–OH⁻	Intractable	
(24)	PbO$_2$–Et$_2$O	(29)	60
(25)	PbO$_2$–Et$_2$O	Intractable	
(26)	PbO$_2$–Et$_2$O	Intractable	

are apparent. Each of the hydroxy-acids (15), (21), and (24) was converted by lead dioxide into the corresponding spiro-dienone (16), (28), or (29), in progressively increasing yield. The formation of an organolead complex (30) provides a reasonable rationale for this reaction.[17] The free phenoxylium ion mechanism of (18) seems less probable but cannot be excluded.

Surprisingly, the ketones (28) and (29) each show only one i.r. band due to the dienone group. *p*-Aryloxy-dienones commonly show a doublet in this region, whereas *ortho*-derivatives have only a single absorption band.[18] The u.v. spectra show intense absorption at *ca.* 300 nm. characteristic of *ortho*-dienones,[19] but the usefulness of this as a means of characterisation has been criticised [20] for the case of dienones bearing a phenoxy-substituent.

As anticipated from the lead dioxide oxidations, lead tetra-acetate is even more effective in inducing cyclisation. Thus, while lead dioxide oxidation of the acid (21) required at least 3 hr. to produce a 40% yield of the dienone (29), lead tetra-acetate effected the same transformation in 50% yield after only 15 min. The involvement of the lead triacetate derivative (31) or its isomer (32), with the latter favoured in the absence of significant amounts of acetoxylated products, is implied.

Contrary to expectations, the reactions of the ethyl esters (19) and (22) did not parallel those of the parent acids. No products could be isolated from the lead dioxide oxidation of the ester (19), but similar treatment of the mono-t-butylated compound (22) gave a nearly quantitative yield of the non-crystalline spiro-benzoxet (33). This structure was confirmed by reductive acetylation, which gave the dibenzofuran (34), characterised by abnormally low field t-butyl resonances in its

[14] C. H. Hassall and A. I. Scott, 'Chemistry of Natural Phenolic Compounds,' Pergamon, London, 1961, p. 119.
[15] D. H. Hey and W. A. Waters, *Chem. Rev.*, 1937, **21**, 169.
[16] C. G. Haynes, A. H. Turner, and W. A. Waters, *J. Chem. Soc.*, 1956, 2823.
[17] W. von E. Doering, M. Farber, and A. Sayigh, *J. Amer. Chem. Soc.*, 1952, **74**, 4370.

[18] K. Dimroth, H. Perst, K. Schlömer, K. Worschech, and K.-H. Müller, *Chem. Ber.*, 1967, **100**, 629.
[19] J. Derkosch and W. Kaltenegger, *Monatsh.*, 1957, **88**, 778.
[20] E. Müller, K. Ley, and G. Schlechte, *Chem. Ber.*, 1957, **90**, 2660; F. R. Hewgill and B. S. Middleton, *J. Chem. Soc.* (*C*), 1967, 2316.

n.m.r. spectrum,[21,22] and the oily hydroxy-acetate (35). These results are similar to those encountered during the oxidation of 4-methoxy-2-t-butylphenol and the subsequent reactions of the product.[21,23] Formation of the spiro-compound probably involves phenoxyl radicals, at least in the initial carbon–carbon coupling of the phenolic nuclei.

mechanism for this reaction is suggested (Scheme 2), on the basis of ample precedent from earlier p-alkyl-phenol oxidations,[24] but many other possibilities exist.
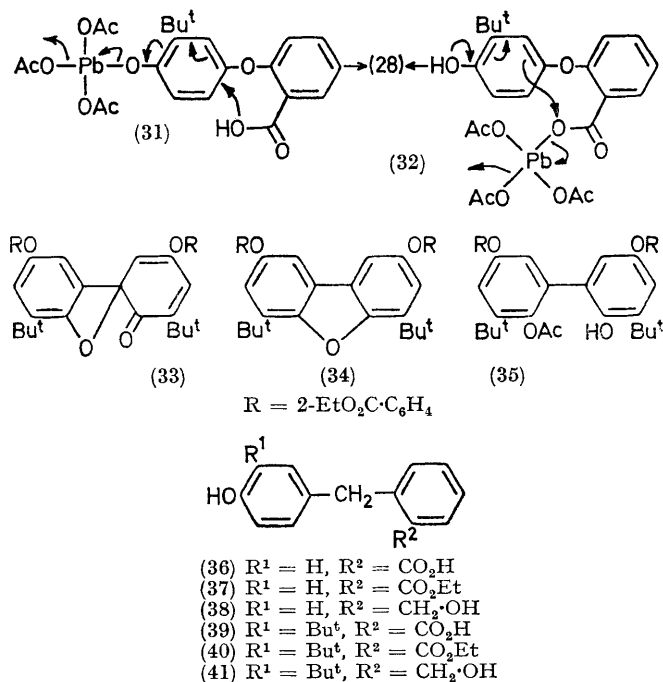
In contrast, the t-alkylated hydroxy-acid (39) was oxidised in low yield to a spiro-dienone (43). Two i.r. absorptions (at 1643 and 1670 cm.$^{-1}$) attributable to
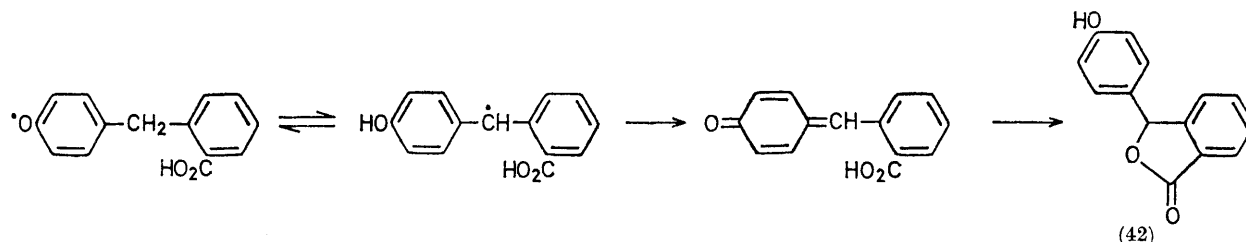
SCHEME 2

The benzyl alcohols (20), (23), and (26) gave intractable products after exposure to lead dioxide, and this also was the case when the alcohol (20) was oxidised by potassium ferricyanide. This suggests a free-radical process where, as well as the possibility of inter-molecular coupling, there is the added potential complication of radical-induced hydrogen abstraction from the benzylic methylene group.

An extension of the investigation to the diphenyl-methane derivatives (36)—(41) produced the results
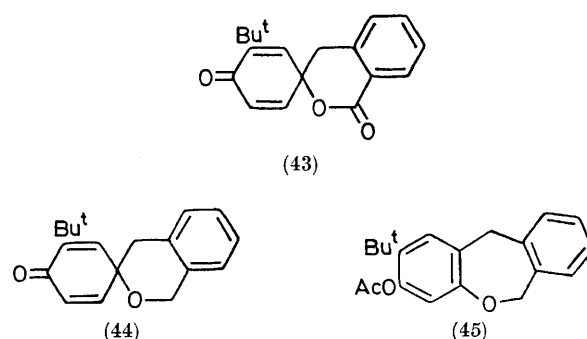
the dienone system were present, contrary to the case mentioned earlier for the oxa-dienones (28) and (29). There appears to be no simple rationale for the distinctly different behaviour of the acids (36) and (39)

TABLE 3

Oxidation of diphenylmethane derivatives

Substrate	Reagent	Product	Yield (%)
(36)	PbO$_2$–Et$_2$O	(42)	60
	Fe(CN)$_6$$^{3-}$	(42)	7·5
(39)	PbO$_2$–Et$_2$O	(43)	10
(40)	Pb(OAc)$_4$–PhH	Intractable	
(41)	Pb(OAc)$_4$–PhH	(44)	50

with the possible exception that the t-butyl group of (39) might hinder the phenolic hydroxy-group to lead dioxide attack. This would then favour the formation of a carboxylate complex [cf. (32)] and hence of the spiro-dienone.

The heterolytic nature of lead tetra-acetate oxidations is supported by the conversion of the benzyl alcohol (41) into the spiro-product (44), also probably via an organo-

(31) (32)

(33) (34) (35)

R = 2-EtO$_2$C·C$_6$H$_4$

(36) R^1 = H, R^2 = CO$_2$H
(37) R^1 = H, R^2 = CO$_2$Et
(38) R^1 = H, R^2 = CH$_2$·OH
(39) R^1 = Bu^t, R^2 = CO$_2$H
(40) R^1 = Bu^t, R^2 = CO$_2$Et
(41) R^1 = Bu^t, R^2 = CH$_2$·OH

shown in Table 3. Oxidation of the hydroxy-acid (36) by either lead dioxide or potassium ferricyanide produced not a spiro-dienone, but the phthalide (42). A

(43)

(44) (45)

lead complex. The structure of this non-crystalline dienone (44) was confirmed when it rearranged, in acetic anhydride with boron trifluoride catalysis, to the crystalline oxepin (45).

In conclusion, we have not yet demonstrated a

[21] F. R. Hewgill and D. G. Hewitt, J. Chem. Soc. (C), 1967, 726.
[22] D. G. Hewitt, Chem. Comm., 1970, 227.
[23] F. R. Hewgill and B. R. Kennedy, J. Chem. Soc. (C), 1966, 362.

[24] C. D. Cook and B. Norcross, J. Amer. Chem. Soc., 1956, 78, 3797; R. H. Bauer and E. M. Coppinger, Tetrahedron, 1963, 19, 1201; C. D. Cook and N. D. Gilmour, J. Org. Chem., 1960, 25, 1429.

phenoxylium ion coupling process between two phenolic nuclei. However, for some substrate–reagent combinations ionic mechanisms more adequately explain the products from phenol oxidations.

EXPERIMENTAL

M.p.s were determined with a micro-hot-stage apparatus. I.r. and u.v. spectra were recorded by Unicam SP 200 and 800 spectrometers, respectively. N.m.r. spectra were recorded for solutions in deuteriochloroform with tetramethylsilane as internal standard, with a Varian A60 spectrometer. Unless otherwise noted, silica gel was used as the adsorbent for preparative t.l.c.

Derivatives of Bis-2-hydroxy-1-naphthylmethane.—(a) *Monobenzyl ether* (5). The monosodium salt of the naphthol [25] (21·6 g.) and benzyl chloride (8·6 g., 1 mol.) were heated in refluxing ethanol (100 ml.) for 2 hr. The solution was then diluted with water and extracted with ether. Evaporation of the dried (Na_2SO_4) extracts left a red oil (23·6 g.), which crystallised on trituration with ethanol to give the *monobenzyl ether* (5) (10·5 g.), prisms, m.p. 151—151·5° (from ethanol), $\lambda_{max.}$ ($CHCl_3$) 272sh (log ε 3·96), 282 (4·06), 293 (4·02), 323 (3·64), and 334 nm. (3·73), $\nu_{max.}$ (Nujol) 3450 cm.$^{-1}$ (OH), τ 4·73 (O·CH_2Ph), 5·20 (ArCH_2Ar'), and 8·47 (OH) (Found: C, 86·2; H, 5·8. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·7%).

(b) *Mono-4-nitrobenzyl ether* (6). Similar treatment of the salt (3·24 g.) with *p*-nitrobenzyl chloride (1·69 g.) gave the *mononitrobenzyl ether* (1·45 g.) as yellow prisms, m.p. 182—184°, $\lambda_{max.}$ ($CHCl_3$) 271 (log ε 4·39), 280 (4·39), 291sh (4·27), 319 (3·75), and 334 nm. (3·80), $\nu_{max.}$ (Nujol) 3500 cm.$^{-1}$ (OH) (Found: C, 77·2; H, 4·9; N, 2·9. $C_{28}H_{21}NO_4$ requires C, 77·2; H, 4·9; N, 3·2%).

Oxidation of Bis-2-hydroxy-1-naphthylmethane (2).—(a) *By sodium bismuthate.* The naphthol (130 mg.) in benzene (15 ml.) was shaken with sodium bismuthate (131 mg.) for 3 hr. The mixture was then washed with water, dried (Na_2SO_4), and evaporated to leave the spironaphthalenone (3) (120 mg.), m.p. 170—171° (lit.,[8] 171—172°).

(b) *By cerium*(IV). The naphthol (1 g.) in acetone (50 ml.) was added slowly to a stirred solution of cerium(IV) hydroxide (1 g.) in 2N-sulphuric acid (200 ml.). The product was then extracted into ether. T.l.c. showed only immobile material with no indication of the presence of any naphthalenone (3).

Oxidation of 2-Hydroxy-1-naphthyl-(2-methoxy-1-naphthyl)-methane (4).—(a) *By potassium ferricyanide.* The monomethyl ether [26] (1 g.) in ether (75 ml.) was added to a stirred solution of potassium ferricyanide (2·1 g.) and sodium hydroxide (5 g.) in water (200 ml.). The product (0·9 g.) gave 1-(2-methoxy-1-naphthylmethyl)-1-[1-(2-methoxy-1-naphthylmethyl)-2-naphthyloxy]naphthalene-2(1H)-one (9) as pale yellow prisms, m.p. 136—138° (decomp.; sealed capillary) (from benzene–ether) $\lambda_{max.}$ ($CHCl_3$) 276sh (log ε 4·15), 286 (4·25), 297 (4·25), 323 (4·12), and 336 nm. (3·97), $\nu_{max.}$ (Nujol) 1680 cm.$^{-1}$ (αβ-unsaturated C=O), τ 6·17 and 6·62 (2 × OMe), 6·17 (ArCH_2R), and 5·17 (ArCH_2Ar') (Found: C, 84·1; H, 5·7%; M, 632. $C_{44}H_{24}O_4$ requires C, 84·3; H, 5·5%; M, 627).

This product was quantitatively reduced by zinc in acetic acid to the starting material (4), m.p. and mixed m.p. 148—150°.

(b) *By cerium*(IV). A solution of cerium(IV) ammonium sulphate (2·1 g.) in water (50 ml.) was added during 15 min. to a stirred mixture of the monomethyl ether (0·5 g.) in chloroform (25 ml.) and potassium carbonate (2 g.) in water (100 ml.). After 7·5 hr. unchanged naphthol (4) (0·8 g.) was recovered.

(c) *By manganese dioxide.* The monoether (0·2 g.) in benzene (10 ml.) was shaken with manganese dioxide (2 g.) for 16 hr., giving the dimer (9) (0·2 g.), m.p. 133—135°.

(d) *By tetraethylammonium periodate.* Tetraethylammonium periodate [27] (336 mg.) and the naphthol (316 mg.) were dissolved in methanol (50 ml.). After 72 hr. the dimeric ketone (9) (106 mg.), m.p. 133—135°, had crystallised. T.l.c. of the mother liquors showed them to contain almost pure monomethyl ether, contaminated with a trace of the dimer.

(e) *By lead tetra-acetate.* The monoether (1·0 g.) and lead tetra-acetate (2 g.) were stirred in benzene (75 ml.) for 3 hr. The solution was then washed with water, dried (Na_2SO_4), and evaporated to leave a yellow gum. Recrystallisation from benzene–light petroleum afforded 1-acetoxy-1-(2-methoxy-1-naphthylmethyl)naphthalene-2(1H)-one (13) (0·8 g.) as pale yellow prisms, m.p. 134—136°, $\lambda_{max.}$ (EtOH) 275infl. (log ε 3·90), 284 (4·02), 295 (4·07), 313 (3·97), and 333infl. nm. (3·81), $\nu_{max.}$ (Nujol) 1680 (αβ-unsaturated C=O) and 1745 cm.$^{-1}$ (acetate), τ 6·36 (ArCH_2R), 6·64 (OMe), and 8·07 (OAc) (Found: C, 77·3; H, 5·4. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%).

Oxidation of 2-Benzyloxy-1-naphthyl-(2-hydroxy-1-naphthyl)methane (5).—(a) *By potassium ferricyanide.* Oxidation of the monobenzyl ether (1 g.) as described for compound (4) gave 1-(2-benzyloxy-1-naphthylmethyl)-1-[1-(2-benzyloxy-1-naphthylmethyl)-2-naphthyloxy]naphthalene-2(1H)-one (10) (0·9 g.), yellow prisms, m.p. 149—155°, $\lambda_{max.}$ ($CHCl_3$) 276sh (log ε 4·22), 286 (4·32), 298 (4·31), 323 (4·12), and 336 nm. (4·07), $\nu_{max.}$ (Nujol) 1690 cm.$^{-1}$ (αβ-unsaturated C=O), τ 5·32 (ArCH_2Ar'), 6·04 (ArCH_2R), and 4·82 and 5·12 (2 × O·CH_2Ph) (Found: C, 86·1; H, 5·5. $C_{56}H_{42}O_4$ requires C, 86·35; H, 5·4%).

The naphthalenone (10) (100 mg.) was heated at 100° with zinc dust (200 mg.) in acetic acid (10 ml.) for 10 min. The mixture was then diluted with ether, washed thoroughly with water, dried (Na_2SO_4), and evaporated to leave starting material (5) (90 mg.), m.p. 150—151°.

(b) *By sodium bismuthate.* The naphthol (112 mg.) in benzene (15 ml.) was shaken with sodium bismuthate (140 mg.) for 3 hr. Evaporation of the solvent left the dimer (10) (100 mg.), m.p. 148—153°.

(c) *By manganese dioxide.* The monoether (0·2 g.) in benzene (20 ml.) was shaken with manganese dioxide (2 g.) for 16 hr. Filtration and evaporation of the solvent left the dimer (10) (0·18 g.), m.p. 148—153°.

(d) *By tetraethylammonium periodate.* Tetraethylammonium periodate (400 mg.) and the monobenzyl ether (395 mg.) were dissolved in methanol (50 ml.). After 72 hr. pure dimer (10) (143 mg.) had separated from solution. T.l.c. of the mother liquors showed them to contain almost pure starting material with a little of the dimer.

(e) *By cerium*(IV). Oxidation of the monobenzyl ether (500 mg.) in ether (100 ml.) by cerium(IV) ammonium sulphate (2 g.) in water (100 ml.) gave a gum. Preparative

[25] W. J. Evans and S. Smiles, *J. Chem. Soc.*, 1937, 727.
[26] R. S. Corley and E. R. Blout, *J. Amer. Chem. Soc.*, 1947, **69**, 755.
[27] A. K. Qureshi and B. Sklarz, *J. Chem. Soc. (C)*, 1966, 412.

t.l.c. of a sample (63 mg.) gave unchanged naphthol (22 mg.) and the dimer (10) (35 mg., 85%).

(f) *By chromium trioxide.* The naphthol (180 mg.) and chromium trioxide (0·5 g.) were dissolved in dry pyridine (50 ml.). After 15 min. the solution was diluted with water; ether extracted the dimer (10) (155 mg.), m.p. 148—153°.

(g) *By nitrous acid.* Acetic acid (10 ml.) was added to a solution of the monoether (213 mg.) in benzene (50 ml.) and sodium nitrite (2 g.) in water (100 ml.) under nitrogen. Work-up after 30 min. gave the naphthalenone (10) (160 mg.).

(h) *By thallium*(III) *acetate.* The naphthol (210 mg.), thallium(III) acetate [28] (0·5 g.) in benzene (75 ml.), and acetic acid (5 ml.) were stirred for 2·5 hr. Chromatography of the product (227 mg.) on silica gel gave unchanged naphthol (20 mg.), the dimer (10) (42 mg.), and pale yellow prisms of 1-*acetoxy*-1-(2-*benzyloxy*-1-*naphthylmethyl*)*naphthalene*-2(1H)-*one* (12) (102 mg.), m.p. 128—130° (from benzene–light petroleum), $\lambda_{max.}$ (EtOH) 247infl. (log ε 3·97), 285 (4·11), 295 (4·15), 310 (4·04), and 333infl. nm (3·86), $\nu_{max.}$ (Nujol) 1680 (αβ-unsaturated C=O) and 1745 cm.$^{-1}$ (acetate), τ 6·27 (ArCH$_2$R), 8·07 (OAc), and 5·16 and 5·52 (doublets, *J* 12 Hz, O·CH$_2$Ph) (Found: C, 80·4; H, 5·3. C$_{30}$H$_{24}$O$_4$ requires C, 80·3; H, 5·4%).

(i) *By lead tetra-acetate.* The monoether (1·0 g.) and lead tetra-acetate (2 g.) in benzene (75 ml.) were stirred for 15 hr. Evaporation of the washed solution left the acetoxynaphthalenone (12) (1·1 g.), m.p. 128—130°.

Oxidation of 2-Hydroxy-1-naphthyl-(2-p-nitrobenzyloxy-1-naphthyl)methane (6).—(a) *By potassium ferricyanide.* The mono-*p*-nitrobenzyl ether (200 mg.) in chloroform (20 ml.) was oxidised by potassium ferricyanide (350 mg.) and sodium hydroxide (500 mg.) in water (50 ml.) during 1 hr. Recrystallisation of the product from benzene gave 1-[2-(*p*-*nitrobenzyloxy*)-1-*naphthylmethyl*]-1-[1-(2-*p*-*nitrobenzyloxy*-1-*naphthylmethyl*)-2-*naphthyloxy*]*naphthalen*-2(1H)-*one* (11) as yellow prisms, m.p. 168—170° $\lambda_{max.}$ (CHCl$_3$) 274 (log ε 4·63), 284 (4·63), 296sh (4·52), 319sh (4·22), and 333sh nm (4·13), $\nu_{max.}$ (Nujol) 1680 cm.$^{-1}$ (αβ-unsaturated C=O) (Found: C, 77·4; H, 4·6; N, 2·95%; *M*, 826. C$_{56}$H$_{40}$N$_2$O$_8$ requires C, 77·4; H, 4·6; N, 3·2%; *M*, 869).

(b) *By manganese dioxide.* Oxidation of the monoether (0·2 g.) as described for the monobenzyl ether gave the dimeric naphthalenone (11), m.p. and mixed m.p. 167—170°.

(c) *By tetraethylammonium periodate.* Tetraethylammonium periodate (200 mg.) and the mono-ether (200 mg.) were dissolved in methanol (30 ml.). After 72 hr. pure dimer (90 mg.), m.p. 167—170°, had crystallised. T.l.c. of the mother liquors showed them to contain almost pure starting material.

Ethyl 2-(4-Hydroxyphenoxy)benzoate (19).—2-(4-Hydroxyphenoxy)benzoic acid [13] (0·5 g.) was heated in refluxing ethanol (10 ml.) containing concentrated sulphuric acid (0·2 ml.) for 15 hr. Dilution with water and extraction with ether gave the *hydroxy-ester* (19) (0·4 g.) as plates, m.p. 90—91°, $\nu_{max.}$ (Nujol) 3400 (OH) and 1695 cm.$^{-1}$ (ester), τ 4·07 (OH), 5·82 (q, *J* 7·0 Hz, CH$_2$), and 8·70 (t, *J* 7·0 Hz, CH$_3$) (Found: C, 69·6; H, 5·45. C$_{15}$H$_{14}$O$_4$ requires C, 69·75; H, 5·5%).

2-(4-Hydroxyphenoxy)benzyl Alcohol (20).—The ethyl ester (19) (0·7 g.) and lithium aluminium hydride (0·5 g.) were heated in refluxing ether (30 ml.) for 2 hr. Evapor-

ation of the washed and dried (Na$_2$SO$_4$) solution left the *benzyl alcohol* (20) (0·45 g.), as plates, m.p. 113—114°, $\nu_{max.}$ (Nujol) 3250 and 3480 cm.$^{-1}$ (OH), τ 6·58 (ArOH), 1·55 (ROH), and 5·72 (partially resolved q, CH$_2$·O) (Found: C, 72·0; H, 5·5. C$_{13}$H$_{12}$O$_3$ requires C, 72·2; H, 5·6%).

t-Butylation of 2-(4-Hydroxyphenoxy)benzoic Acid (15).—Concentrated sulphuric acid (5 ml.) in acetic acid (15 ml.) was added to a stirred solution of the hydroxy-acid (2·3 g.) and t-butyl alcohol (3 g.) in acetic acid (50 ml.). After 2 hr. at 100° the solution was diluted with ether, washed thoroughly with water, dried (Na$_2$SO$_4$) and evaporated, leaving *2-hydroxy-3-t-butylxanthone* (27) (1 g.), m.p. 218—221°, $\lambda_{max.}$ (EtOH) 245 (log ε 4·66), 304 (3·84), and 368 nm (3·84), $\nu_{max.}$ (Nujol) 1630, 1650, 1660sh (C=O), and 3400 cm.$^{-1}$ (OH), τ 8·52 (Bu^t) and 0·80 (OH) (Found: C, 76·1; H, 6·2. C$_{17}$H$_{16}$O$_3$ requires C, 76·1; H, 6·0%); the *acetate* gave prisms, m.p. 154—156°, $\nu_{max.}$ (Nujol) 1620, 1640, 1670 (C=O), and 1765 cm.$^{-1}$ (acetate), τ 8·57 (Bu^t), 7·62 (OAc), and 2·26 and 2·47 (2 × ArH) (Found: C, 73·4; H, 5·6. C$_{19}$H$_{18}$O$_4$ requires C, 73·5; H, 5·85%).

t-Butylation of Ethyl 2-(4-Hydroxyphenoxy)benzoate (19).—Concentrated sulphuric acid (20 ml.) was added slowly to a stirred solution of the hydroxy-ester (2·4 g.) and t-butyl alcohol (6 ml.) in acetic acid (50 ml.). After several hours the solution was diluted with water and extracted with ether. The product (2·8 g.) was adsorbed on alumina (60 g.; grade III). Benzene–light petroleum eluted *ethyl 2-(4-hydroxy-2,5-di-t-butylphenoxy)benzoate* (25), as plates (0·2 g.), m.p. 157—159°, $\nu_{max.}$ (Nujol) 1710 (ester) and 3450 cm.$^{-1}$ (OH), τ 8·67 and 8·69 (2 × Bu^t), 3·24 (2 × ArH), 4·95 (OH), 5·60 (q, *J* 7 Hz, CH$_2$), and 8·66 (t, *J* 7 Hz, CH$_3$) (Found: C, 74·6; H, 8·1. C$_{23}$H$_{30}$O$_4$ requires C, 74·6; H, 8·2%).

Benzene eluted *ethyl 2-(4-hydroxy-3-t-butylphenoxy)benzoate* (22) (0·9 g.), as plates, m.p. 148·5—149·5°, $\nu_{max.}$ (Nujol) 1710 (ester) and 3420 cm.$^{-1}$ (OH), τ 8·63 (Bu^t), 4·60 (OH), 5·66 (q, *J* 7 Hz, CH$_2$), and 8·69 (t, *J* 7 Hz, CH$_3$) (Found: C, 72·6; H, 6·9. C$_{19}$H$_{22}$O$_4$ requires C, 72·6; H, 7·05%).

2-(4-Hydroxy-3-t-butylphenoxy)benzoic Acid (21).—The ethyl ester (22) (460 mg.) and sodium hydroxide (0·2 g.) were heated in a refluxing mixture of water (10 ml.) and ethanol (20 ml.) for 1·5 hr. The solution was then poured into dilute aqueous sulphuric acid and extracted with ether. The *hydroxy-acid* (21) (330 mg.) was obtained as prisms (from acetone–light petroleum), m.p. 216—218° $\nu_{max.}$ (Nujol) 1690 (C=O) and 3450 cm.$^{-1}$ (OH) (Found: C, 71·05; H, 6·1. C$_{17}$H$_{18}$O$_4$ requires C, 71·3; H, 6·3%).

Similar hydrolysis of ethyl 2-(4-hydroxy-2,5-di-t-butylphenoxy)benzoate (25) (208 mg.) gave 2-(4-*hydroxy-2,5-di-t-butylphenoxy*)*benzoate* (24) (173 mg.), m.p. 223—224° (from acetone–light petroleum) $\nu_{max.}$ (Nujol) 1680 (C=O) and 3450 cm.$^{-1}$ (OH), τ 8·71 (2 × Bu^t) and 3·15 and 3·39 (2 × ArH) (Found: C, 73·5; H, 7·8. C$_{21}$H$_{26}$O$_4$ requires C, 73·7; H, 7·7%).

2-(4-Hydroxy-3-t-butylphenoxy)benzyl Alcohol (23).—The ethyl ester (22) (330 mg.) and lithium aluminium hydride (0·4 g.) were heated in refluxing ether for 3 hr. The product afforded the *benzyl alcohol* (23) (240 mg.) as needles, m.p. 79—80° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3440 cm.$^{-1}$ (OH), τ 8·64 (Bu^t), 4·60 (ArOH), 7·58 (ROH), and 5·22 (CH$_2$·O) (Found: C, 75·0; H, 7·4. C$_{17}$H$_{20}$O$_3$ requires C, 75·0; H, 7·4%).

In a similar manner ethyl 2-(4-hydroxy-2,5-di-t-butylphenoxy)benzoate (85 mg.) gave the *benzyl alcohol* (26) (80 mg.), m.p. 148—150°, $\nu_{max.}$ (Nujol) 3380 and 3580 cm.$^{-1}$

[28] E. Hecker and R. Lattrell, *Annalen*, 1963, **662**, 48.

(OH) (Found: C, 76·7; H, 8·3. $C_{21}H_{28}O_3$ requires C, 76·8; H, 8·6%).

Lead Dioxide Oxidation of Ethyl 2-(4-Hydroxyphenoxy)-benzoate (19).—The hydroxy-ester (207 mg.) and lead dioxide (5 g.) were shaken in ether (50 ml.) for 25 hr. T.l.c. showed the presence of one major product and the complete absence of starting phenol (19). Evaporation of the filtered solution left a yellow gum (46 mg.) which rapidly decomposed to a red oil. T.l.c. of this material showed only a streak, with no discrete spots.

Oxidation of 2-(4-hydroxyphenoxy)benzyl alcohol (20) (200 mg.) under similar conditions gave a low yield (22 mg.) of a colourless gum, indicated by t.l.c. to be a mixture of at least five compounds. This was not further investigated.

Oxidation of 2-(4-Hydroxy-3-t-butylphenoxy)benzoic Acid (21).—(a) *By lead dioxide.* The hydroxy-acid (200 mg.) and lead dioxide (2 g.) were shaken in ether (50 ml.) for 3 hr. The solution was then filtered, washed with saturated aqueous sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated to leave a yellow gum (115 mg.). Preparative t.l.c. gave pale yellow prisms of 3'-*t*-butylspiro-[1,3-*benzodioxan*-2,1'-*cyclohexa*-2',5'-*diene*]-4,4'-*dione* (28), m.p. 69—70°, $\nu_{max.}$ (Nujol) 1685 (αβ-unsaturated C=O) and 1745 cm.$^{-1}$ (lactone C=O), $\lambda_{max.}$ (EtOH) 238sh (log ε 4·12) and 300 nm (3·44), τ 8·73 (Bu^t), and 3·77, 3·03, and 3·20 (ABX system, J_{AB} 10, J_{BX} 3 Hz, 3 × olefinic H) (Found: C, 71·9; H, 5·9. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%).

(b) *By lead tetra-acetate.* The hydroxy-acid (76 mg.) and lead tetra-acetate (0·4 g.) were stirred together in benzene (10 ml.) for 15 min. Evaporation of the washed solution left the spiro-dienone (28) (37·6 mg.), m.p. 69—70°.

Lead Dioxide Oxidation of Ethyl 2-(4-Hydroxy-3-t-butyl-phenoxy)benzoate (22).—The hydroxy-ester (343 mg.) and lead dioxide (2·5 g.) were shaken in ether (50 ml.) for 1·5 hr. Evaporation of the filtered suspension left a pale red gum (338 mg.), which did not crystallise. T.l.c. showed the presence of only one compound which absorption spectra indicated to be 4,5'-bis-(2-ethoxycarbonylphenoxy)-3',6-di-t-butylspiro[benzoxet-2,1'-cyclohexa-3',5'-dien]-2'-one (33), $\nu_{max.}$ (film) 1660 (αβ-unsaturated C=O and 1720 cm.$^{-1}$ (ester), τ 8·53 and 8·71 (2 × Bu^t), 4·33 and 4·56 (doublets, J 1 Hz, 2 × olefinic H), and peaks due to two dissimilar ethyl ester groups.

The oxidation product (33) (0·5 g.) was treated with zinc dust (1 g.) and sodium acetate (0·1 g.) in refluxing acetic anhydride (20 ml.) for 0·5 hr. The oily product (400 mg.) was separated into two components by preparative t.l.c., first on silica gel and then on alumina. The faster-moving component was recrystallised from aqueous acetic acid to give 2,8-*bis*-(2-*ethoxycarbonylphenoxy*)-4,6-*di*-*t*-*butyldibenzo*-*furan* (34) as plates, m.p. 109—110°, $\nu_{max.}$ (Nujol) 1710 and 1725 cm.$^{-1}$ (ester), τ 8·41 (2 × Bu^t), 5·76 (q, J 7 Hz, 2 × CH_2), and 8·74 (t, J 7 Hz, 2 × CH_3) (Found: C, 74·8; H, 6·7. $C_{38}H_{40}O_7$ requires C, 75·0; H, 6·6%).

The slower-moving component failed to crystallise but it was probably 2-acetoxy-5,5'-bis-(2-ethoxycarbonylphenoxy)-2'-hydroxy-3,3'-di-t-butylbiphenyl (35), $\nu_{max.}$ 1710 and 1720 (ester), 1760 (acetate), and 3550 cm.$^{-1}$ (OH), τ 8·62 and 8·68 (2 × Bu^t), 5·02 (OH), 6·45 (OAc), and peaks due to two dissimilar ethyl groups.

Oxidation of 2-(4-Hydroxy-3-t-butylphenoxy)benzyl Alcohol

²⁹ W. Baker, D. Clark, W. D. Ollis, and T. S. Zeally, *J. Chem. Soc.*, 1952, 1452.

(23).—(a) *By lead dioxide.* Oxidation of the phenol (280 mg.) in ether (50 ml.) by lead dioxide (2 g.) for 4 hr. gave a black gum. T.l.c. analysis showed mainly immobile material and no discrete products.

(b) *By potassium ferricyanide.* The phenol (180 mg.) in ether (50 ml.) was shaken with potassium ferricyanide (0·6 g.) and sodium hydroxide (0·6 g.) in water (100 ml.) for 0·5 hr. The ether layer developed an intense red-brown colour. Evaporation of the ether solution left a dark brown gum which slowly became yellow. T.l.c. showed only immobile material, and the i.r. spectrum showed hydroxy- but not carbonyl absorption.

Lead Dioxide Oxidation of 2-(4-Hydroxy-2,5-di-t-butyl-phenoxy)benzoic Acid (24).—The hydroxy-acid (89 mg.) in ether (50 ml.) was treated with lead dioxide (1 g.) for 1 hr. Work-up as usual gave 2',5'-*di*-*t*-*butylspiro*-[1,3-*benzodioxan*-2,1'-*cyclohexa*-2',5'-*diene*]-4,4'-*dione* (29) (54 mg., 60%) as pale yellow needles (from benzene–light petroleum), m.p. 171—172°, $\nu_{max.}$ (Nujol) 1680 (αβ-unsaturated C=O) and 1745 cm.$^{-1}$ (lactone C=O), $\lambda_{max.}$ (EtOH) 230 (log ε 4·26) and 297 nm. (3·43), τ 8·65 and 8·88 (2 × Bu^t), and 3·31 and 3·72 (olefinic H) (Found: C, 74·1; H, 7·0. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·1%).

Similar oxidations of 2-(4-hydroxy-2,5-di-t-butylphen-oxy)benzyl alcohol (26) and ethyl 2-(4-hydroxy-2,5-di-t-butylphenoxy)benzoate (25) gave intractable mixtures.

Ethyl 2-(4-Hydroxybenzyl)benzoate (37).—2-(4-Hydroxy-benzyl)benzoic acid ²⁹ (10·2 g.) was esterified by refluxing ethanol (100 ml.) containing sulphuric acid (0·5 ml.) during 24 hr. The *product* (10·5 g.) was obtained as plates (from carbon tetrachloride–light petroleum), m.p. 52—54°, $\nu_{max.}$ (Nujol) 1695 (ester) and 3420 cm.$^{-1}$ (OH), τ 5·76 ($ArCH_2Ar'$), 5·77 (q, J 7 Hz, CH_2), and 8·77 (t, J 7 Hz, CH_3) (Found: C, 74·95; H, 6·55. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%).

Lithium aluminium hydride reduced this ester (3·3 g.) to the corresponding *benzyl alcohol* (38) (2·4 g.), m.p. 124—125° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3250 and 3450 cm.$^{-1}$ (OH), τ 6·08 ($ArCH_2Ar'$) and 5·42 ($ArCH_2O$) (Found: C, 78·7; H, 6·5. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%).

Ethyl 2-(4-Hydroxy-3-t-butylbenzyl)benzoate (40).—Concentrated sulphuric acid (10 ml.) was slowly added to a solution of ethyl 2-(4-hydroxybenzyl)benzoate (7·8 g.) and t-butyl alcohol (3·5 g.) in acetic acid (100 ml.). After 20 hr. at room temperature, water was added and the product was extracted into ether. The extract was washed with saturated aqueous sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue (9 g.) was dissolved in light petroleum and adsorbed on alumina (100 g.; grade III). Light petroleum eluted a little non-crystalline material. Further elution with light petroleum and then benzene gave *ethyl 2-(4-hydroxy-3-t-butylbenzyl)benzoate* (40) (6·9 g., 70%), which crystallised from light petroleum as prisms, m.p. 78·5—79·5°, $\nu_{max.}$ (Nujol) 1695 (ester) and 3490 cm.$^{-1}$ (OH), τ 8·65 (Bu^t), 8·69 (t, J 7 Hz, CH_3), 5·70 (q, J 7 Hz, CH_2), 5·71 ($ArCH_2Ar'$), 4·97 (OH), and 3·50, 3·23 and 2·92 (ABX system, J_{AB} 8, J_{BX} 2 Hz, 3 × ArH) (Found: C, 76·7; H, 8·0. $C_{20}H_{24}O_3$ requires C, 76·9; H, 7·7%).

Basic hydrolysis of this ester (40) (1·04 g.) and recrystallisation of the product from benzene–light petroleum gave 2-(4-*hydroxy*-3-*t*-*butylbenzyl*)*benzoic acid* (39) (0·75 g.), as plates, m.p. 145·5—146·5°, $\nu_{max.}$ (Nujol) 1682 and 1695 (C=O), and 3560 cm.$^{-1}$ (OH) (Found: C, 75·9; H, 7·0. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·1%).

Lithium aluminium hydride in refluxing ether reduced the ester (1·0 g.) to the corresponding *benzyl alcohol* (41) (0·70 g.), m.p. 98·5—99° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3450 cm.$^{-1}$ (OH), $\lambda_{max.}$ (EtOH) 231 (log ε 3·94), 280 (3·43), and 286sh nm (3·39), τ 8·64 (Bu^t), 6·05 (ArCH$_2$Ar'), 5·39 (ArCH$_2$·O), 4·52 (ArOH), 8·17 (ROH), and 3·59, 3·42, and 2·97 (ABX system, J_{AB} 8, J_{BX} 2 Hz, 3 × ArH) (Found: C, 80·2; H, 8·2. C$_{18}$H$_{22}$O$_2$ requires C, 80·0; H, 8·2%).

Oxidation of 2-(4-Hydroxybenzyl)benzoic Acid (36).—(a) *By lead dioxide.* The hydroxy-acid (108 mg.) and lead dioxide (1 g.) were stirred in ether (50 ml.) for 24 hr. The product was isolated as usual and recrystallised from benzene–light petroleum giving 3-(4-hydroxyphenyl)-phthalide (42) (65 mg.), m.p. 154—155°, identical (mixed m.p.) with an authentic sample prepared by reduction of 2-(4-hydroxybenzoyl)benzoic acid.[30]

(b) *By potassium ferricyanide.* The hydroxy-acid (1·2 g.) in ether (30 ml.) was stirred with aqueous potassium ferricyanide (3·3 g., 2 mol.) in saturated aqueous sodium hydrogen carbonate solution (50 ml.) for 4 hr. The ether layer was then separated, dried, and evaporated to leave the phthalide (42) (91 mg., 7·5%), m.p. 153—155°.

Lead Dioxide Oxidation of 2-(4-Hydroxy-3-t-butylbenzyl)-benzoic Acid (39).—Oxidation of the hydroxy-acid (114 mg.) by lead dioxide (0·5 g.) in the usual manner gave *3,4-di-hydro-3'-t-butylspiro-[2-benzopyran-3,1'-cyclohexa-2',5'-di-ene]-1,4'-dione* (43) (11·5 mg., 10%) as plates, m.p. 147—148° (from methanol), $\nu_{max.}$ (Nujol) 1643 and 1670 (dienone), and 1710 cm.$^{-1}$ (lactone), τ 6·78 (partially resolved q, ArCH$_2$R), 8·77 (Bu^t), and 3·87 (d, J 10 Hz, olefinic H)

[30] W. R. Orndorff and L. Kelley, *J. Amer. Chem. Soc.*, 1922, **44**, 1518.

(Found: C, 76·4; H, 6·4. C$_{18}$H$_{18}$O$_3$ requires C, 76·6; H, 6·4%).

Lead Tetra-acetate Oxidation of Ethyl 2-(4-Hydroxy-3-t-butylbenzyl)benzoate (40).—The ester (102 mg.) in benzene (10 ml.) was stirred with lead tetra-acetate (0·4 g.) for 15 min. Chromatography of the product showed the presence of at least three compounds but the spiro-dienone (43) was absent.

Lead Tetra-acetate Oxidation of 2-(4-Hydroxy-3-t-butyl-benzyl)benzyl Alcohol (41).—Oxidation of the phenol (113 mg.) in the normal manner, followed by preparative t.l.c., yielded 3,4-dihydro-3'-t-butylspiro-[2-benzopyran-3,1'-cyclohexa-2',5'-dien]-4'-one (44) (58 mg.) as an oil which failed to crystallise, $\nu_{max.}$ (film) 1644 and 1670 cm.$^{-1}$ (dienone), τ 8·78 (Bu^t), 7·27 and 6·94 (doublets, J 16 Hz, ArCH$_2$R), 5·08 (ArCH$_2$·O), and 3·93, 3·22, and 3·37 (ABX system, J_{AB} 10, J_{BX} 3 Hz, 3 × olefinic H).

Boron trifluoride–ether complex (5 drops) was added to a solution of this dienone (44) (62 mg.) in acetic anhydride (10 ml.). After 15 min. the solution was poured into water and extracted with ether. Preparative t.l.c. afforded a gum (30 mg.) and *3-acetoxy-2-t-butyldibenz*[b,e]*oxepin* (45) (15 mg.) needles, m.p. 190·5—192°, $\lambda_{max.}$ (EtOH) 208 (log ε 4·37), 232sh (3·67), 279 (3·29), and 287 nm. (3·27), $\nu_{max.}$ (Nujol) 1756 cm.$^{-1}$ (acetate), τ 8·70 (Bu^t), 7·69 (OAc), 5·83 (ArCH$_2$Ar'), 4·73 (ArCH$_2$·O), 3·26 and 3·19 (singlets, 2 × ArH), and 2·77 (4 × ArH) (Found: C, 77·3; H, 7·0. C$_{20}$H$_{22}$O$_3$ requires C, 77·4; H, 7·1%).