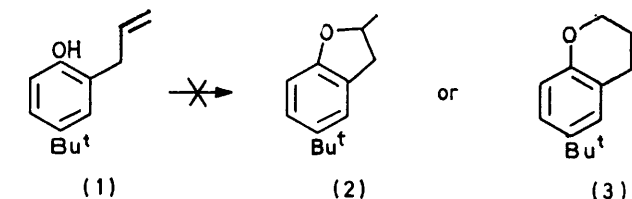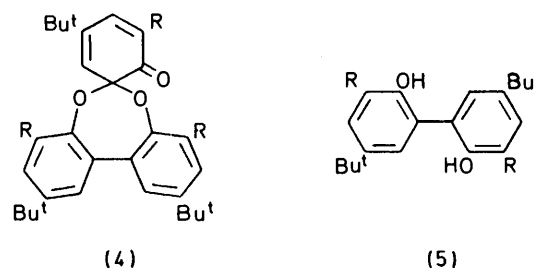# Oxidation of Phenols. Part 5.[1] Oxidation of 2-Allyl-4-t-butylphenol

By **David T. Dalgleish, Norman P. Forrest, Derek C. Nonhebel,*** and **Peter L. Pauson,*** Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland

Oxidation of 2-allyl-4-t-butylphenol with manganese(III) acetylacetonate afforded the spiroacetal (4). There was no evidence for products arising from intramolecular attack of the phenoxyl radical centre on the double bond of the allyl group. The reaction of 2-allyl-4-t-butylphenol with vanadium oxide trichloride gave 2-allyl-4-chlorophenol and 2-allyl-4,6-dichlorophenol. The reactions of several other phenols with vanadium oxide trichloride in which chlorodealkylation is a common feature are also reported.

PREVIOUS studies have failed to distinguish unequivocally between a homolytic and heterolytic mechanism for the photochemical addition of phenols to alkenes to give alkyl aryl ethers.[2,3] This problem has been further studied by examining the reaction of 2-naphthyloxyl and p-t-butylphenoxyl radicals, generated by oxidation of phenols with manganese(III) acetylacetonate,[4] with cyclohexene. The main product in each case was the C–C coupled dimer, *i.e.* 1,1'-bi-2-naphthol or 5,5'-di-t-butylbiphenyl-2,2'-diol, respectively. The reaction with 2-naphthyloxyl radicals yielded a trace of cyclohexyl 2-naphthyl ether, but none of the corresponding product was obtained with p-t-butylphenoxyl radicals. The absence of a significant yield of the alkyl aryl ether [2] in these reactions suggests that their formation in the photochemical process does not involve free phenoxyl radicals. The reaction of phenoxyl radicals with a double bond should be more favoured when both the radical centre and the double bond are in the same molecule. To this end the oxidation of 2-allyl-4-t-butylphenol (1) with manganese(III) acetylacetonate was examined to see if the coumaran (2), or possibly the chroman (3), would be produced: the analogous photochemical reaction gave a fairly good yield of the coumaran.[2] None of either of

(1)   (2)   or   (3)

these products was obtained in this oxidation or in oxidations with alkaline potassium hexacyanoferrate(III) or with silver carbonate on Celite. The main product in each case was the spiroacetal (4; R = CH$_2$·CH:CH$_2$), the structure of which follows from its spectral characteristics (see Experimental section). Analogous products have been reported in the oxidations of 2-methyl-4-t-butyl-

phenol, 2-methoxy-4-t-butylphenol and 2- and 3-alkyl-4-methoxyphenols.[5-8] A trace of a second product, believed to be 3,3'-diallyl-5,5'-di-t-butylbiphenyl-2,2'-diol (5; R = CH$_2$·CH:CH$_2$) on the basis of the similarity of its R_F value to that of 3,3'-dimethyl-5,5'-di-t-butyl-biphenyl-2,2'-diol (5; R = Me) was also formed.

(4)   (5)

Oxidation of 2-methyl-4-t-butylphenol gave a mixture of the spiroacetal (4; R = Me) and the biphenyldiol (5; R = Me), and 2,4-di-t-butylphenol gave the biphenyldiol (5; R = Bu^t). Oxidation of a mixture of the biphenyl-diol (5; R = Me) and 2-methyl-4-t-butylphenol gave the spiroacetal (4; R = Me) in greater yield than could have been obtained just from oxidation of 2-methyl-4-t-butyl-phenol. This suggests that the spiroacetal arises from cross-coupling of phenoxyl radicals derived from the mono- and bis-phenols, followed by further oxidation of the resultant trimeric species (6) as indicated in the Scheme. This contrasts with the mechanism proposed by Hewgill for the formation of the spiroacetal from the C–O dimer (7): he suggests that initial C–O coupling occurs.[9] The absence of any trimeric product from 2,4-di-t-butylphenol is probably a reflection of steric hindrance to further reaction. That no ether is detected from these oxidations is certainly consistent with the mechanism proposed.

In the oxidation of β-naphthol in cyclohexane or benzene with manganese(III) acetylacetonate a small quantity of a trimeric product was also isolated. This was identified on the basis of spectral data as the spiro-acetal (8).

In a further attempt to induce formation of a coumaran from oxidation of 2-allyl-4-t-butylphenol, we employed vanadium oxide trichloride, which has been reported to

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[2] W. M. Horspool and P. L. Pauson, *Chem. Comm.*, 1967, 195.
[3] D. T. Dalgleish, D. C. Nonhebel, and P. L. Pauson, *J. Chem. Soc. (C)*, 1971, 1174.
[4] M. J. S. Dewar and T. Nakaya, *J. Amer. Chem. Soc.*, 1968, **90**, 7134.
[5] D. F. Bowman and F. R. Hewgill, *Chem. Comm.*, 1967, 471; *J. Chem. Soc. (C)*, 1971, 1777.
[6] F. R. Hewgill, *J. Chem. Soc.*, 1962, 4987.
[7] F. R. Hewgill and B. S. Middleton, *J. Chem. Soc.* 1965, 2914.
[8] D. F. Bowman, F. R. Hewgill, and B. R. Kennedy, *J. Chem. Soc. (C)*, 1966, 2274.
[9] F. R. Hewgill and D. G. Hewitt, *Tetrahedron Letters*, 1965, 3737.

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be an efficient intramolecular oxidant.[10-12] The only products isolated were 2-allyl-4-chlorophenol (9) and 2-allyl-4,6-dichlorophenol (10); none of the cyclized products were detected. The same products, in the ratio of 2 : 1, were obtained from the reaction of *o*-allyl-phenol, and also from the reaction of 2-allyl-4-methyl-phenol. In this last case the extent of reaction was much less and 2-chloro-4-methylphenol was also obtained, together with two unidentified dimeric products. In contrast little reaction occurred between *p*-t-butylphenol and vanadium oxide trichloride: the only identified

mercial materials and were recrystallized or redistilled before use. 2-Allyl-4-t-butyl- and 2-allyl-4-methyl-phenol were prepared by Claisen rearrangement of the appropriate allyl *p*-alkylphenyl ether.

Oxidation of 2-Naphthol with Manganese(III) Acetylaceton-ate in Cyclohexene.—A solution of 2-naphthol (7.21 g, 0.05 mol) and manganese(III) acetylacetonate (17.3 g, 0.05 mol) in cyclohexene (420 ml) was refluxed under nitrogen for 20 h. The manganese(II) acetylacetonate was filtered off and the filtrate washed with sodium disulphite solution, to reduce any remaining manganese(III) acetylacetonate, and with water. The solvent was distilled off and the
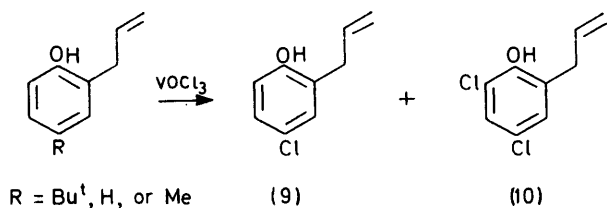

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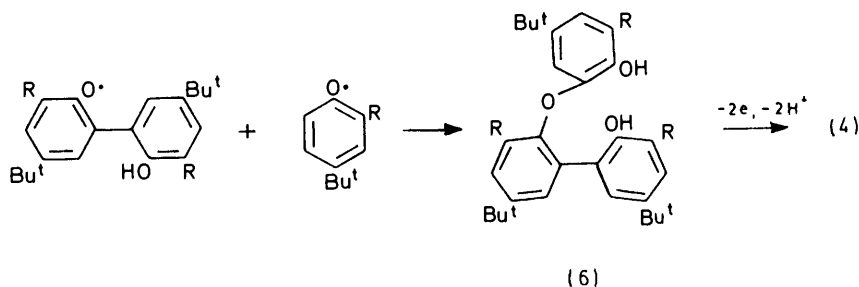
SCHEME

product was *p*-chlorophenol. The only product charac-terized from the reaction of *p*-cresol was the *o,o'*-coupled

(7)　　　　　　　(8)
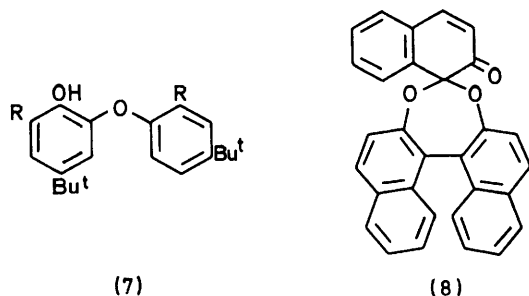
bis-phenol, 5,5'-dimethylbiphenyl-2,2'-diol. A much greater degree of reaction occurred with 2,4-di-t-butyl-phenol, which afforded 4-chloro-2-t-butylphenol, 2-chloro-4,6-di-t-butylphenol, and 2,6-dichloro-4-t-butylphenol.

R = Bu[t], H, or Me　　(9)　　　(10)

It thus appears that for this substitution of alkyl groups by chlorine atoms to occur a group in the *ortho*-position is advantageous, and that the extent of reaction is greatest when this is an allyl group.

EXPERIMENTAL

Starting Materials.—*p*-t-Butylphenol, 2,4-di-t-butyl-phenol, 2-naphthol, *o*-allylphenol, and *p*-cresol were com-

residue in ether was extracted with dilute sodium hydroxide (3 × 50 ml) and then with water before drying. The neutral layer was evaporated; the residue (1.78 g) was shown by t.l.c. on silica [2% ethyl acetate in benzene as eluant] to contain a trace of cyclohexyl 2-naphthyl ether. Addition of a small amount of ether to this material resulted in the precipitation of a solid (0.18 g), which was recrystallized from methylene chloride–light petroleum to give yellow crystals of *spiro[dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2,1'-(2'H)-naphthalen]-2'-one* (8), m.p. 245° (decomp.) (Found: M^+, 426.12526. $C_{30}H_{18}O_3$ requires M, 426.12558); $v_{max.}$ (KCl) 1 685 cm^{-1} (CO); τ (CDCl$_3$) 1.75—3.05 (16 H, m, aromatic), 3.32 (1 H, d, :CH, J 9 Hz), and 3.77 (1 H, d, :CH, J 9 Hz).

Acidification of the alkaline extracts afforded a mixture of 2-naphthol and 1,1'-bi-2-naphthol; these were separated by chromatography on silica.

Oxidation of p-t-Butylphenol with Manganese(III) Acetyl-acetonate in Cyclohexene.—The reaction was carried out as above with *p*-t-butylphenol (7.4 g, 0.05 mol). T.l.c. showed the presence of 5,5'-di-t-butylbiphenyl-2,2'-diol. No *p*-t-butylphenyl cyclohexyl ether was detected.

Oxidation of 2-Allyl-4-t-butylphenol.—(a) *With manganese-(III) acetylacetonate.* A mixture of 2-allyl-4-t-butylphenol (4.75 g, 0.025 mol) and manganese(III) acetylacetonate (8.8 g, 0.025 mol) in acetonitrile (300 ml) was refluxed under nitrogen for 30 h, filtered, diluted with ether (300 ml), and washed successively with 10% sodium disulphite solution and water. The dried organic layer was evaporated and the residue (4.7 g) was chromatographed on silica. Elution with 6 : 1 light petroleum–ether gave a yellow oil. Addition of methanol to this precipitated 4',5,8'-triallyl-2',3,10'-tri-t-butylspiro[cyclohexa-2,4-diene-1,6'-dibenzo[d,f][1,3]dioxe-pin]-6-one (4; R = CH$_2$·CH:CH$_2$) (1.2 g, 25%), which gave yellow crystals (from methanol), m.p. 151—152° (Found:

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[10] W. L. Carrick, G. L. Karapinka, and G. J. Kwiatkowski, *J. Org. Chem.*, 1969, **34**, 2388.

C, 82.8; H, 8.5%; M^+, 564.3585. $C_{39}H_{48}O_3$ requires C, 82.9; H, 8.6%; M, 564.3603); $\nu_{max.}$ (CCl$_4$) 1 690 cm^{-1} (CO); τ (CDCl$_3$) 2.53—2.80 (4 H, m, aromatic), 3.04 (1 H, m, :CH), 3.87 (1 H, m, :CH, J 3 Hz), 3.9—4.26 (3 H, m, :CH·CH$_2$), 4.66—5.07 (6 H, m, CH:CH$_2$), 6.69 (4 H, d, CH$_2$, J 7 Hz), 6.85 (2 H, d, CH$_2$, J 7 Hz), 8.63 (18 H, s, Bu^t), and 8.82 (9 H, s, Bu^t). Elution with 2 : 1 light petroleum–benzene gave a mixture of 2-allyl-4-t-butylphenol and an unidentified compound, probably 3,3'-diallyl-5,5'-di-t-butyl-biphenyl-2,2'-diol as it had an R_F value on t.l.c. similar to that of 3,3'-dimethyl-5,5'-di-t-butylbiphenyl-2,2'-diol.

(b) *With potassium hexacyanoferrate*(III). Potassium hexacyanoferrate(III) (6.38 g, 0.02 mol) in 0.4M-sodium carbonate (25 ml) was added over 20 min to a solution of 2-allyl-4-t-butylphenol (3.8 g, 0.02 mol) in 0.4M-sodium carbonate (100 ml). The mixture was stirred for 2 h and worked up as previously described.[13] T.l.c. showed the product to consist mainly of the dioxepin (4; R = CH$_2$·CH:CH$_2$), with traces of 2-allyl-4-t-butylphenol and the same unidentified compound as above.

(c) *With silver carbonate on Celite*. A mixture of 2-allyl-4-t-butylphenol (4.75 g, 0.025 mol) and silver carbonate on Celite (14.25 g, equiv. to 0.025 mol Ag$^+$) in benzene (300 ml) was refluxed under nitrogen for 2 h. The mixture was filtered, the filtrate evaporated, and the residue steam distilled. The ultimate residue was analysed by t.l.c. and shown to have a composition similar to that obtained in the oxidation with hexacyanoferrate.

Oxidation of 2-Methyl-4-t-butylphenol.—(a) *With silver carbonate on Celite.* The reaction was carried out as above with 2-methyl-4-t-butylphenol (4.1 g, 0.025 mol) and worked up as described above. Chromatography of the crude product (3.37 g) on silica (2 : 1 light petroleum–benzene as eluant) gave the dioxepin (4; R = Me) (1.8 g, 44%), m.p. 239—240° (lit.,[5] 238—240°) (yellow prisms from methanol). Elution with 1 : 1 light petroleum–benzene gave 3,3'-dimethyl-5,5'-di-t-butylbiphenyl-2,2'-diol (0.87 g, 21%), m.p. 111—112° (lit.,[5] 115—116°). Further elution with 1 : 1 light petroleum–benzene and benzene gave mixtures of the bisphenol and unchanged 2-methyl-4-t-butylphenol.

(b) *With manganese*(III) *acetylacetonate*. The reaction was carried out as for 2-allyl-4-t-butylphenol but with 2-methyl-4-t-butylphenol (4.1 g, 0.025 mol). T.l.c. of the product on silica (1 : 1 light petroleum–benzene as eluant) showed that this consisted of the dioxepin (4; R = Me), the bisphenol (5; R = Me), and 2-methyl-4-t-butylphenol. Chromatography gave the dioxepin (4; R = Me) (0.91 g, 22%).

Oxidation of a Mixture of 2-Methyl-4-t-butylphenol and 3,3'-Dimethyl-5,5'-di-t-butylbiphenyl-2,2'-diol.—A mixture of the phenol (0.057 8 g, 0.35 mmol), the bis-phenol (0.115 g, 0.35 mmol), and manganese(III) acetylacetonate (0.373 g, 1.05 mmol) in acetonitrile (12.5 g) was refluxed for 5 h and worked up as above to afford the dioxepin (4; R = Me) (0.068 g), m.p. and mixed m.p. 237—239°.

Oxidation of 2,4-Di-t-butylphenol with Manganese(III) *Acetylacetonate.*—2,4-Di-t-butylphenol (5.15 g, 0.025 mol) and manganese(III) acetylacetonate (8.8 g, 0.025 mol) in acetonitrile (300 ml) were refluxed for 5 h and the product was worked up as above. The residue (5.4 g) was extracted with methanol. The insoluble material (2.07 g) was recrystallized from methanol to give 3,3',5,5'-tetra-t-butyl-biphenyl-2,2'-diol, m.p. 199—200° (lit.,[14] 200—201°). The methanol-soluble fraction was shown by t.l.c. to consist of this bisphenol and unchanged 2,4-di-t-butylphenol.

Reaction of Vanadium Oxide Trichloride with Phenols.—A solution of the phenol (0.025 mol) in ether (500 ml) was added dropwise over 1 h to a solution, at -78 °C, prepared by addition of vanadium oxide trichloride [15] (19.8 g, 0.21 mol) to ether (500 ml) at $-78°$. The colour of the solution immediately changed from deep red to deep blue and then to brown. Hydrogen chloride was evolved. The mixture was maintained at -78 °C for a further 2 h, then allowed to warm to room temperature, and left at this temperature overnight. It was then refluxed for 10 h, washed with water, dried, and evaporated. The residue was examined by g.l.c. on columns of (A) 2.5% silicone gum rubber on silanised Celite at 160 °C, (B) 2.5% silicone grease XE 60 on silanised Celite at 170 °C, or (C) 10% Carbowax on Chromosorb G at 100 °C, or by t.l.c. on silica plates (20 : 1 benzene–ethyl acetate as eluant).

(a) *Reaction of 2-allyl-4-t-butylphenol.* The crude mixture was chromatographed on silica. Elution with 50 : 1 light petroleum–ether gave 2-allyl-4,6-dichlorophenol, b.p. 110—112° at 2 mmHg (lit.,[16] 264° at 759 mmHg) (Found: C, 53.4; H, 4.7. Calc. for $C_9H_8Cl_2O$: C, 53.2; H, 4.5%); $\nu_{max.}$ (liq.) 3 520 cm^{-1} (OH); τ (CDCl$_3$) 2.72 (1 H, d, aromatic, J 3 Hz), 2.90 (1 H, d, aromatic, J 3 Hz), 3.78—4.20 (1 H, m, CH:CH$_2$), 4.37 (1 H, s, OH), 4.72—4.96 (2 H, m, CH:CH$_2$), and 6.57 (2 H, d, CH$_2$, J 7 Hz). Continued elution with this solvent gave 2-allyl-4-chlorophenol, b.p. 97—98° at 2 mmHg (lit.,[17] 124—125° at 12 mmHg) (Found: C, 64.2; H, 5.6. Calc. for C_9H_9ClO: C, 64.1; H, 5.4%); $\nu_{max.}$ (liq.) 3 430 cm^{-1} (OH); τ (CDCl$_3$) 2.70—3.28 (3 H, m, aromatic), 3.75—4.18 (1 H, m, CH:CH$_2$), 4.67—4.97 (2 H, m, CH:CH$_2$), 4.90 (1 H, s, OH), and 6.63 (2 H, d, CH$_2$, J 7 Hz), identical (spectra) with an independently synthesized sample.

(b) *Reaction of 2-allylphenol.* The crude product (4.3 g) was chromatographed on silica. Elution with 1 : 1 light petroleum–benzene gave 2-allyl-4,6-dichlorophenol. Continued elution gave 2-allyl-4-chlorophenol. G.l.c. analysis (column A) of the crude mixture showed that the ratio of the two phenols was 1 : 2.

(c) *Reaction of 2-allyl-4-methylphenol.* G.l.c. analysis (column A) of the product showed the presence of 2-chloro-4-methylphenol, 2-allyl-4,6-dichlorophenol, 2-allyl-4-methyl-phenol and 2-allyl-4-chlorophenol in the ratios 1 : 2 : 12 : 1.

(d) *Reaction of p-cresol.* The crude product was shown by g.l.c. (column B) to contain p-cresol, traces of 5,5'-di-methylbiphenyl-2,2'-diol, and unidentified polymeric material.

(e) *Reaction of p-t-butylphenol.* The product was shown (g.l.c. on column C) to consist predominantly of p-t-butyl-phenol, with a trace of p-chlorophenol.

(f) *Reaction of 2,4-di-t-butylphenol.* G.l.c. analysis (column A) of the product indicated that the main component was 2,4-di-t-butylphenol. Lesser amounts of 2-chloro-4,6-di-t-butylphenol, 2,6-dichloro-4-t-butylphenol, and 4-chloro-2-t-butylphenol were obtained. These were synthesized for comparison by reactions of sulphuryl chloride with 2,4-di-t-butylphenol, p-t-butylphenol, and o-t-butylphenol, respectively.

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