The Oxidation of 2,4-Di-t-butylphenol by Copper–Amine Complexes

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Summary Revised structures are presented for some copper-catalysed oxidation products of 2,4-di-t-butylphenol.

KNOWLEDGE of the mechanism of the oxidation of phenols by copper–amine complexes is vital to an understanding of the properties of phenol-oxidising enzyme systems (*e.g.* laccase, tyrosinase).[1] As a preliminary step in this direction a recent series of investigations[2] by Karpov and his colleagues is of interest.

Oxidation of 2,4-di-t-alkylphenols by the system [O_2–CuCl or $CuCl_2$–morpholine or –piperidine] was reported[2a] to produce products of type (**1**). Intrigued by these unusual structures we have repeated the oxidation of 2,4-di-t-butylphenol by [O_2–CuCl–morpholine] and find the product to be more adequately represented by structure (**2**)† [m.p. 152°; i.r. (CCl_4) 1695 ($C{=}O$), 2500—3500 cm.$^{-1}$ (bonded OH); n.m.r. $\tau(CCl_4)$, 9·08, 8·82, 8·73, 8·65 (36H, 4 x Bu^t), 7·38 (4H, multiplet, $\cdot CH_2NCH_2\cdot$), 6·23 (4H, multiplet, $\cdot CH_2OCH_2\cdot$), 3·87, 3·50 (2H, doublets, *J* 2·5 Hz, $=CH$),

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† All new compounds had satisfactory elemental analyses.

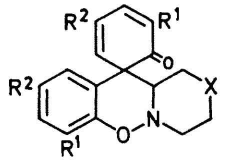
2·92, 3·18 (2H, doublets *J* 2·5 Hz, ArH), and −0·75 (1H, bonded OH, exchanged slowly by D_2O); u.v. (MeOH) 276, 320, and 375sh nm (log ϵ 3·62, 3·42 and 3·24)].

Structure (**2**) accounts for the reported[2a] chemical reactions, the *o*-quinoid u.v. spectrum,[3] the single i.r. carbonyl band,[4] the broad OH stretching band in the i.r. spectrum, complemented by a low-field (τ − 0·75) exchangeable peak in the n.m.r. spectrum, and the presence of an exceptionally high-field (τ 9·08) t-butyl resonance due to a t-butyl group on an *sp*^{3} carbon.[5] Nearly all the significant peaks in the mass spectrum are explained in the chart and the transitions shown are all supported by appropriate meta-stable peaks. Comparison of the reported[2a] properties of the other oxidation products (**1**) indicates that they also should be assigned structures related to (**2**).

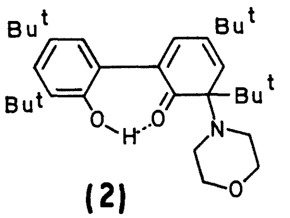
$$\begin{tikzcd}
480\ (54\%) & M^+\ 495\ (62\%) \arrow[l, "-\bullet\mathrm{CH}_3"'] \arrow[dl, "-\bullet\mathrm{C}_4\mathrm{H}_9"'] \arrow[r, "-\mathrm{C}_4\mathrm{H}_9\mathrm{NO}"] & 408\ (26\%) \arrow[r, "-\mathrm{C}_4\mathrm{H}_8"] \arrow[dl, "-\bullet\mathrm{CH}_3"'] \arrow[d, "-\bullet\mathrm{C}_4\mathrm{H}_9"] & 352\ (100\%) \arrow[d, "-\bullet\mathrm{CH}_3"] \\
438\ (38\%) & 393\ (10\%) & 351\ (100\%) & 337\ (90\%)
\end{tikzcd}$$

CHART

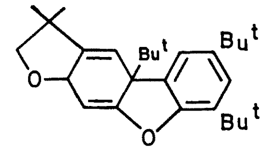
Mass spectrum (70 ev, 200°) of (**2**)



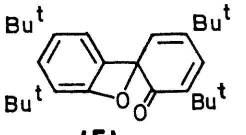
(1) R^1, R^2 = t-alkyl
X = CH_2, O



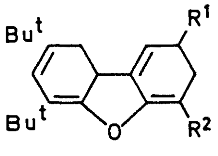
(2)



(4)



(5)



(3) R^1 = OMe, R^2 = Bu^t
(6) R^1 = Bu^t, R^2 = OH
(7) R^1 = Bu^t, R^2 = OMe

Treatment of the morpholino-dienone (**2**) with hydrochloric acid in methanol gave the known[6] methoxydibenzofuran (**3**), a reaction not readily rationalised on the basis of formulation (**1**; $R^1 = R^2 = Bu^t$, X = O).

The Russian workers[2b] stated that oxidation of 2,4-di-t-butylphenol by [O_2–CuCl-pyridine–KOH] gave a compound of 'probable' structure (**4**), described as being inert to hydrogen at 150 atm. in the presence of palladised charcoal, to lithium aluminium hydride, and to hydroiodic and hydrobromic acids. In our hands several attempts to repeat this oxidation produced only the known benzoxet (**5**). This compound was recently reported as being converted into the methoxydibenzofuran (**3**) by methanolic hydrochloric acid.[6] We have confirmed this and that a second compound is also formed, and this we find to be the hydroxydibenzofuran (**6**)† [m.p. 116—117°; n.m.r. τ (CCl_4), 8·55, 8·61, 8·43 (27H, 3 x Bu^t), 3·83 (1H, broad, OH), 2·22, 2·53, 2·62, and 2·97 (4H, doublets, *J* 2 Hz, ArH); u.v. (MeOH), 212, 252, 260, 276infl, 282, 299, and 310 nm (log ϵ 4·55, 3·96, 4·08, 3·89, 4·10, 3·67, and 3·64), (MeOH + NaOH) 209, 243, 268sh, 280sh, 288, and 312 nm (log ϵ 4·55, 4·51, 4·03, 4·00, 4·12, and 3·80); i.r. (CCl_4) 3700 cm.$^{-1}$ (OH)]. Methylation of the phenol (**6**) gave a second methoxydibenzofuran (**7**)† [m.p. 103—105°; n.m.r. τ (CCl_4) 8·56, 8·57, 8·40 (27H, 3 x Bu^t), 5·90 (3H, OMe), 2·27, 2·65 (2H, doublets, *J* 2 Hz, ArH), 2·52, and 3·06 (2H, doublets, *J* 1·5 Hz, ArH); u.v. (MeOH) 225, 251, 259, 276infl, 284, 298, and 309 nm (log ϵ 4·66, 4·06, 4·19, 3·98, 4·19, 3·72, and 3·68)]. The structures of the dibenzofurans follow unequivocally from their mode of preparation and their spectra.[7]

Dibenzofuran (**3**) has a melting point and n.m.r. spectrum closely similar to those ascribed[2b] to compound (**4**) and they are apparently the same compound. The mass spectrum reported[2a] for the dimer (**4**) appears to have been obtained from (**3**) contaminated with a trace of the benzoxet (**5**).

Attempts to reproduce the oxidation of 4-t-butylphenol as described[2b] failed completely.

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[1] B. R. Brown, in "Oxidative Coupling of Phenols" eds. W. I. Taylor and A. R. Battersby, Marcell Dekker, New York, 1967, p. 167.

[2] (a) V. V. Karpov, V. A. Puchkov, and M. L. Khidekel, *Zhur. org. Khim.*, 1968, **4**, 1594; (b) V. V. Karpov and M. L. Khidekel, *ibid.*, 1968, **4**, 861; (c) *ibid.*, 1967, **3**, 1669.

[3] J. Derkosch and W. Kaltenegger, *Monatsh.*, 1957, **88**, 778.

[4] K. Dimroth, H. Perst, K. Schlömer, K. Worschech, and K. H. Muller, *Chem. Ber.*, 1967, **100**, 629.

[5] F. R. Hewgill and B. S. Middleton, *J. Chem. Soc.* (*C*), 1967, 2316. Some workers (J. Petranek and J. Pilar, *Coll. Czech. Chem. Comm.*, 1969, **34**, 79) have suggested that this is not a reliable guide because of the existence of exceptions to the "rule" that t-butyl groups on *sp*^{3} carbon absorbs at τ 8·90 or higher (E. C. Horswill and K. U. Ingold, *Canad. J. Chem.*, 1966, **44**, 269). To the knowledge of the present author, the only t-butyl group on an *sp*^{2} carbon which absorbs in this region (τ 9·03) is in an unusual molecular environment in which it is flanked by three oxygen atoms (see F. R. Hewgill and B. R. Kennedy, *J. Chem. Soc.*, 1965, 2921). Recently some *sp*^{3} t-butyl groups absorbing at fields *lower* than τ 8·90 have been reported (T. Matsuura, A. Nishinaga, K. Ogura, and K. Omura, *J. Org. Chem.*, 1969, **34**, 550) but this does not affect the present argument.

[6] H.-D. Becker, *J. Org. Chem.*, 1969, **34**, 1198.

[7] The characteristic low-field (τ 8·42—8·48) resonances of t-butyl groups at C-5 and C-6 of a dibenzofuran have been mentioned before [F. R. Hewgill and D. G. Hewitt, *J. Chem. Soc.* (*C*), 1967, 726]. It would now seem appropriate to extend this range to at least τ 8·37—8·48.