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THE ONE-ELECTRON OXIDATION OF 2-METHOXY-4,6-DI-t-BUTYLPHENOL

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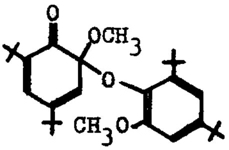
In connection with a program directed toward the systematic study of red-ox behaviour of phenols substituted with bulky alkyl groups we wish to describe in this communication the oxidation of 2-methoxy-4,6-di-t-butylphenol involving a one-electron transfer. The oxidation was carried out by potassium ferricyanide in alkaline medium. This system is known to oxidize the sterically hindered phenols in a one-electron step to phenoxy radicals (1,2).

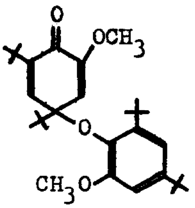
2-Methoxy-4,6-di-t-butylphenol (I) was synthetized by alkylation of 4-t-butylguaiacol with t-butanol and the product was purified by preparative g.l.c. (Apiezon L column), m.p. 27.5-28.5°. Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.27; H, 10.34. The synthesis of I by direct alkylation of guaiacol (3) yields a product containing isomers and the isolation of I in pure state is difficult.

1.15 mmol of I dissolved in 15 ml Claisen solution(KOH, water, methanol in wt.ratio 1:1:2) was oxidized in an atmosphere of N_2 with a solution of 1.2 mmol potassium ferricyanide in 24 ml methanol-water (2:1). The dilution of the reaction mixture with water gave a yellow product in 94% yield. The molecular formula for this compound, m.p. 137-140° (from methanol), was found to be $C_{30}H_{46}O_4$ based on elemental analysis and molecular weight. Anal. Calcd. for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85; Mol.Wt. 470.7. Found: C, 76.70; H, 9.86; Mol.Wt. 464 (in benzene by vapor osmometry). The compound dissolves in nonpolar solvents to a green solution. On heating, the colour of the solution becomes much more intense and turns to blue green. The solution shows an e.s.r. spectrum. The compound has oxidative properties. It liberates iodine (98.8% of equivalent by titration) from a solution of sodium iodide in acetic acid; the product of this reaction was found to be I as estimated by t.l.c. The catalytic hydrogenation (PtO_2) in ethanol yielded the original phenol I as well.

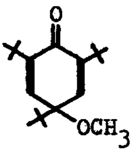
The infrared spectrum (λ_{max}, cm^{-1}: 1672, 1691; absence of OH band) was indicative of a cyclohexadienone structure. We can therefore propose a quinolacetal structure, similar to the structure of the oxidation product of 2-t-butoxy-4,6-di-t-butylphenol studied by Müller et al. (4), with an ether bond in o- (II) or in p- position (III).



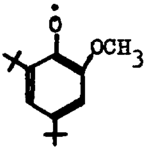
II



III



IV



V

There is no direct proof for distinguishing between II and III at present. The n.m.r. spectrum of the compound seems, however, to favour structure II.

In the n.m.r. spectrum of the oxidation product, the two cyclohexadienone ring protons exhibit a pair of chemically shifted doublets at τ4.57 and 3.22, with a splitting of 2 c/s each, in addition to a broad unresolved band of the aromatic ring protons at τ3.5. (All the lines of the spectrum are broadened, probably due to the presence of free radicals).
A similar pair of doublets is observed in the spectrum of 4,6-di-t-butyl-o-benzoquinone, with τ3.87 and 3.15 and a splitting of 2.4 c/s. Contrary to this, the ring protons of cyclohexadienone IV (modelling structure III) exhibit a singlet at τ3.58. Therefore, the n.m.r. spectrum of the oxidation product seems to favour structure II.

The electron spin resonance spectrum of compound II in benzene solution (FIG.1a) consists of twenty-five equidistant lines.

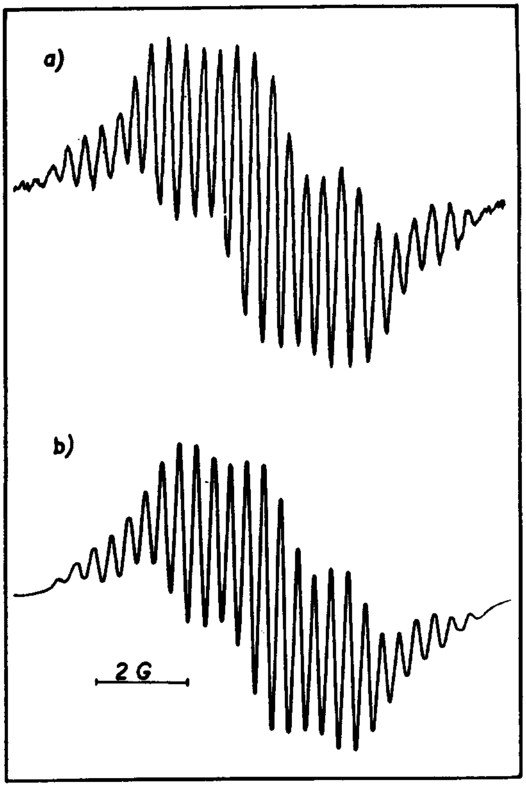


FIG. 1

E.s.r. spectrum of II in benzene
a) experimental - b) simulated

We ascribe this spectrum to the simple phenoxy radical V formed by dissotiation of II. The correctness of this interpretation is supported by the form of the simulated spectrum (FIG. 1b) which was calculated under the assumption that the odd electron is interacting with two nonequivalent ring protons ($a_{H_5} = 1.80 \pm 0.04$ Oe, $a_{H_3} = 0.82 \pm 0.02$ Oe), with three protons of the methoxy group ($a_{H-OCH_3} = 1.48 \pm 0.03$ Oe), with nine protons of the t-butyl group in position 4 ($a_{H-tBu} = 0.38 \pm 0.01$ Oe) and that the line shape is Lorentzian. Values of the splitting constants of 2,4,6-tri-t-butylphenoxyl and 2,6-di-t-butyl-4-methoxyphenoxyl radicals (5,6) confirm this interpretation. By decreasing the concentration of compound II in benzene solution by a factor ten (from 10^{-3}M to 10^{-4}M) the integral intensity of the e.s.r. absorption line decreases only three times. If we raise the temperature of the measured solution, the integral intensity of the absorption line increases at first, and after reaching maximum it decreases due to further reactions of the phenoxy radical.

From the properties mentioned above it follows that the phenoxy radical V primarily formed by the oxidation of phenol I dimerizes, yielding the substituted cyclohexadienone II. This dimer dissociates in solution partially into radicals V. The degree of dissotiation becomes higher in more diluted solution and on rising the temperature. Our further experiments on the oxidation of the 2-alkoxy-4,6-di-t-butylphenols with ethoxy-, isopropoxy- and t-butoxy groups indicate that the products are of similar structure and the course of the oxidation is the same. The degree of dissotiation of dimers in solution into free radicals rises as the alkoxy group of phenol increases.

Our work concerning the detailed study of these dimers and the identification of phenoxy radicals formed, as well as the electrochemical behaviour of these compounds is in progress and the results will be published in full details elsewhere.

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