preparation of the solution; 16 to 18 hr later, the viscosities were measured again. It will be noted from the figure that the viscosity had increased appreciably. The increase in viscosity observed with time appears to arise from formation of aggregates of polymer as well as hydration and change of configuration. Observation by electron microscopy of the aged preparations revealed aggregated particles with a spongy appearance.

The density increment, k_D, was found to be independent of concentration in the range from 0 to 5 g/100 ml. Its measured value was 0.53. Since $k_D = 1 - \bar{v}\rho_0$ (ρ_0 is the density of the solvent, 1.03393 g/ml), $\bar{v}$ is equal to 0.456. It is known that $[\eta] = \nu\bar{v}$, where ν is the viscosity increment. From our data, ν equals 2.9. Einstein demonstrated[2] that ν for a nonhydrated sphere equals 2.5, and deviations from this value are indicative of either hydration or asymmetry. It follows therefore that the iron polymers in freshly prepared solution are behaving as spheres with approximately 7% bound water, by weight. Using the more accurate values for $\bar{v}$ obtained in this work, the molecular weight of the iron hydroxy nitrate polymer from ultracentrifugation measurements is 1.5×10^5, and by direct visualization with electron microscopy is 2.1×10^5. The concentration dependence of reduced specific viscosity observed in Figure 1 is anomalous and is suggestive of polymer–polymer interaction. However, the agreement of molecular weights obtained by sedimentation equilibrium studies on solutions containing 4 g/100 ml of polymer and by electron microscopy of very dilute solutions suggests that the dependence does not arise from aggregation of polymer units.

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(2) A. Einstein, "Investigations on the Theory of the Brownian Movement," Dover Publications, Inc., New York, N. Y., reprinted 1956, pp 49–56.

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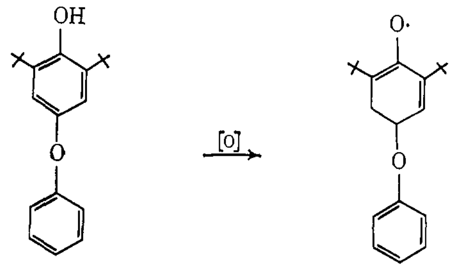
A 4-Phenoxyphenoxy Radical and an Example of Hindered Aryl Ether Rotation

Sir:

The mechanism of the oxidative coupling of phenols has been under study in these laboratories.[1] One of the postulated mechanisms for this reaction involves the transfer of an electron across a diaryl ether bond.[2] This would appear unlikely in a radical reaction because a charge separation must be made with a consequent expenditure of energy. It was with a view toward examining the possibility of such an electron jump that this work was undertaken.

The *o*-alkylation method of Kolka, *et al.*,[3] was used to prepare 4-phenoxy-2,6-di-*t*-butylphenol (I) from *p*-phenoxyphenol and isobutylene. This reaction is slow and required the application of heat to achieve completion. White crystals of I were obtained by recrystallization from hexane, mp 132–133°, in 90% yield. *Anal.* Calcd for $C_{20}H_{26}O_2$: C, 80.5; H, 8.7; mol wt, 298. Found: C, 80.8; H, 8.8; mol wt, 286.

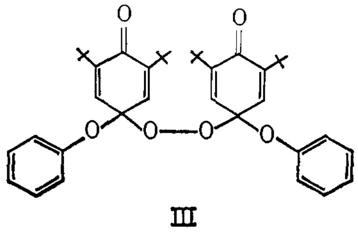
The phenol I could be oxidized to a stable free radical (II), in the absence of oxygen, with a variety of oxidizing agents. The method of choice is alkaline potassium ferricyanide. The esr spectrum of radical II (Figure 1) is a strong triplet due to the coupling of the electron spin to the two *meta* protons on the top ring as shown in the illustration. The splitting constant is 1.05 gauss, which is comparable with 1.8 gauss for tri-*t*-butylphenoxy and 1.0 gauss for 4-*t*-butoxy-2,6-di-*t*-butylphenoxy.[4] The radical is stable in the absence of air and a strong signal could still be obtained from the sample after 6-weeks storage at room temperature. The visible spectrum exhibited a broad maximum at 533 mμ (ε 150).



I II

Two factors argue against any appreciable electron density achieving a "jump" across the aryl ether linkage. There was no detectable interaction of the electron with the hydrogens on the phenoxy ring. The stability of the radical also means that the electron is localized on the hindered ring, otherwise dimerization reactions through the phenoxy ring would be expected.

The radical behaves normally by being converted to the peroxide III when the directions of Cook[5] are followed. A white solid, mp 109–110°, is obtained which has the structure III. *Anal.* Calcd for $C_{40}H_{50}O_6$: C, 76.7; H, 8.0. Found: C, 76.4; H, 7.8.



III

Hydrolysis of this material in 95% ethanol yields phenol and 2,6-di-*t*-butylbenzoquinone. The hydrogen peroxide was not observed.

(1) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959); G. F. Endres and J. Kwiatek, *J. Polymer Sci.*, **58**, 593 (1962).

(2) H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, *SPE Trans.*, **2**, 112 (1962); W. A. Butte, Jr., and C. C. Price, *J. Am. Chem. Soc.*, **84**, 3567 (1962).

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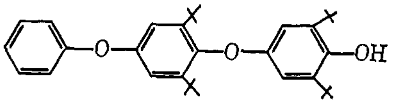
(4) E. Müller, H. B. Stegmann, and K. Scheffler, *Ann.*, **645**, 79 (1961).

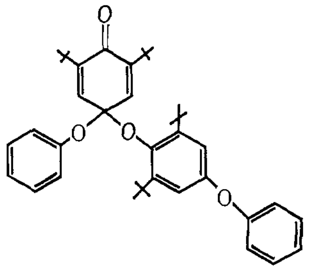
(5) C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 2002 (1956).

When the red solution of the radical II is reduced with acidic iodide solution and the liberated iodine titrated with sodium thiosulfate solution, the correct titer is obtained for the amount of radical corresponding to the original amount of I. However, the products of this reduction are phenol, 4-phenoxy-2,6-di-*t*-butylphenol, and a trimer to which the structure IV is assigned. The amount of these materials obtained is erratic but the usual ratio is 1:2:1.



IV

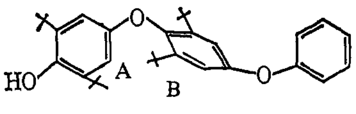
The trimer IV is thought to arise from iodide–acid reduction of the quinone ketal V which probably exists in equilibrium with the radical II. The quinone ketal V has not yet been isolated.



V

The trimer IV is difficult to separate from the phenol I. The samples obtained have been collected from the vapor phase chromatograph. Recrystallization from hexane gave white needles, mp 141°. *Anal.* Calcd for $C_{34}H_{46}O_3$: C, 81.3; H, 9.2; mol wt, 502, Found: C, 81.0; *H*, 9.3; mol wt, 472. The infrared spectrum of the trimer IV is almost identical with that of the phenol I. The chief differences lie in the intensities of various peaks, as might be expected. The nuclear magnetic resonance spectrum offers further support of the structure.

The *t*-butyl groups of the phenol I have a single sharp resonance at τ 8.58 in chloroform. The trimer IV has a sharp resonance at τ 8.80 and a broad resonance at τ 8.60. The peak at higher field is ascribed to the *t*-butyl groups on the B ring. The broad peak is ascribed to the two *t*-butyl groups on the A ring. One group is under the influence of the B ring and the other is not, as illustrated in IV. The hindrance of the *t*-butyl groups on the B ring prevents the A ring from rotating and prevents the *t*-butyls on the A ring from being equivalent. Preliminary examination of the temperature dependence of the nmr spectrum is in agreement with this interpretation.



IV

In summary, it has been found that there is no evidence for any electron density being able to cross the diaryl ether linkage in the radical 4-phenoxy-2,6-di-*t*-butylphenoxyl (II). Additionally, a 2,6-di-*t*-butylphenyl ether has been prepared which exhibits a marked hindrance to rotation about the aryl ether bond.

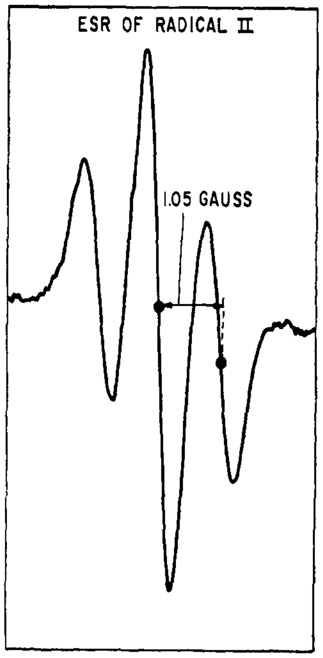


Figure 1.

Acknowledgment. The author wishes to thank Dr. John Lupinski for taking the esr spectrum and Dr. John Bush for taking and helping to interpret the nmr spectra.

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Chemistry of the Streptovaricins. I. Characterization of Streptovaricins A, B, C, D, E, and G

Sir:

Streptovaricin,[1] an orange antibiotic showing marked *in vivo* activity against *Mycobacterium tuberculosis*,[2] has been shown to be a complex of at least five compounds, partially separable by countercurrent distribution[3] and by partition chromatography.[3b,4] The present report describes the properties of the more abundant components, separated by countercurrent distribution and silica gel chromatography, while the accompanying report[5] assigns the structure of the central chromophore of the antibiotics.

Physical and analytical properties of streptovaricins A–E and G are summarized in Table I. Due to the tendency of the streptovaricins to form strong crystal solvates, meaningful analyses were obtained only after precipitating the component from a chlorinated solvent, grinding to a fine powder, and drying under

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