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# SPIN DENSITY DISTRIBUTION IN FREE RADICALS, II (1)

## $O^{17}$-HYPERFINE STRUCTURE OF LABELLED [$O^{17}$]-2,4,6-TRI-TERT.-BUTYL-PHENOXYL

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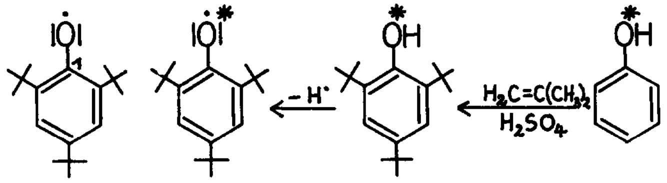
In an earlier publication (2) we have described the distribution of spin density in phenoxy radicals of the type 2,4,6-tri-tert.-butyl-phenoxyl (I).



I II III IV

$\overset{*}{O} = O^{17}$

The values for oxygen and C-atom-1 could be determined only approximately. In particular, the direct proof of a free electron spin density on these two atoms could not be established by esr spectroscopic measurements since naturally occuring $C^{12}$ and $O^{16}$ lack nuclear spins.

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(1) For part I see A. Rieker, K. Scheffler and E. Müller, Liebigs Ann. Chem. 670, 23 (1963).

(2) E. Müller, A. Rieker and K. Scheffler, Liebigs Ann. Chem. 645, 92 (1961).

In order to obtain more information about exact spin density values we synthesized [1-$C^{13}$]-2,4,6-tri-tert.-butyl-phenoxyl (I) and, as formerly described briefly (3), the first $O^{17}$-labelled phenoxy radical, namely [$O^{17}$]-2,4,6-tri-tert.-butyl-phenoxyl (II). The characterization of this latter radical is the subject of this communication.

II was prepared in the following manner. Phenol IV (4), in which the hydroxy oxygen atom is the isotope $O^{17}$, was treated with isobutylene and a catalytic quantity of sulfuric acid in petrolether at 60 - 70°C. The product obtained, [$O^{17}$]-2,4,6-tri-tert.-butyl-phenol (III), was dehydrogenated with leaddioxide in benzene. The separation of small quantities (1 - 10 mg.) of phenol III from polyisobutylene was easily effected with thin-layer chromatography on silica gel ($HF_{254}$/Merck) using a mixture of petrolether/benzene as the eluting solvent. The IR-spectrum of III is distinguishable from that of the unlabelled 2,4,6-tri-tert.-butyl-phenol through a broadening of the OH-stretching vibration at 3665 $cm^{-1}$ and an additional peak at 770 $cm^{-1}$.

The exact determination of the $O^{17}$-content in III and IV was particularly difficult. When IV was converted into 2,4,6-tribromophenol, the mass spectral analysis (5) of the latter compound yielded a $O^{17}$-content of 10%. After conversion of phenol IV into III,

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(3) E. Müller, H. Eggensperger, A. Rieker, K. Scheffler, H.-D. Spanagel, H. B. Stegmann and B. Teissier, Tetrahedron 21, 227 (1965), see Table 1 and footnote, pg. 244. Later K. Dimroth, F. Bär and A. Berndt [Angew. Chemie 77, 217 (1965)] reported another labelled phenoxy radical, [$O^{17}$]-2,4,6-tri-phenyl-phenoxyl.

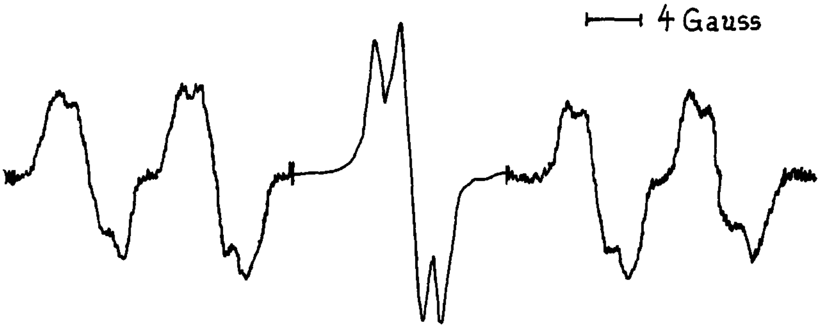
(4) IV is obtained by treating solid phenyldiazoniumchloride in $H_2O^{17}$. We wish to gratefully thank Buchler and Co., Frankfurt/Main and the Yeda Research Co., Rehovoth, Israel for the free supply of small quantities of compound IV.

(5) Conducted in the analytical laboratory of the Yeda Research and Development Co., Rehovoth.

an oxygen content of 6,1 ± 0,1 % $O^{17}$ and 26.3 ± 0,3 % $O^{18}$ was found in III by mass spectral analysis (6). An isotope analysis by means of esr spectroscopy is provided below.

The esr spectrum of our labelled phenoxy radical is clearly explained as the superimposition of the main spectrum (of the unlabelled compound I) upon the spectrum of II. The esr signal of II consists of six components, which are due to the interaction of the free electron with the $O^{17}$-nucleus ($I = 5/2$).

Fig. 1



In the spectrum shown in Fig. 1 the sensitivity of the spectrometer was substantially reduced in the region of the main signal. Consequently, only the four outer O-17 components are recognizable. In other spectra the two inner O-17 components also appear clearly, specifically as shoulders imposed upon the main signal. The coupling constant $a_{O-17}$ equals 10.23 ± 0.1 Gauss. In addition, each of the $O^{17}$-lines is split into a triplet by the meta protons of the aromatic

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(6) We are grateful to Prof.Dr.H.A.Staab and Mr.Ch.Wünsche, Heidelberg, for this analysis.

ring. Due to the non-zero quadrupole moment of the $O^{17}$-nucleus and the consequent related relaxation phenomena, the resolution of this additional hyperfine structure in the case of II is worse than in that of the unlabelled phenoxy radical (main signal).

By comparing the intensity of the $O^{17}$-HFS-lines to the main signal of the unlabelled compound, an enrichment of about 8% in $O^{17}$ is found in compound II. That it is impossible to establish the existence and extent of any oxygen exchange effects in the production of II from IV as starting material results from a comparison of this value from esr measurements with those given above from mass spectral data (namely, 10% $O^{17}$ in IV and 6.1% in III).

From the coupling constant $a_{O-17} = 10.23$ G the proportion of 2s-character equal to 1.25% (7) can be calculated. It is, therefore, experimentally proven for the first time that the free electron in phenoxy radicals possesses a definite spin density on the oxygen atom. In other words, an "oxygen free radical" is here present in accordance with resonance theory. A future communication will describe the influence of various substituents upon the free electron spin density on the oxygen atom.

We wish to thank Professor Dr. Eugen Müller and the Deutsche Forschungsgemeinschaft for making the necessary means available to conduct our research.

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(7) Cf. loc. cit. (3) for the significance of s-character.