

## The E.S.R. Spectra of Some 2,6-Dialkoxyaryloxy Radicals

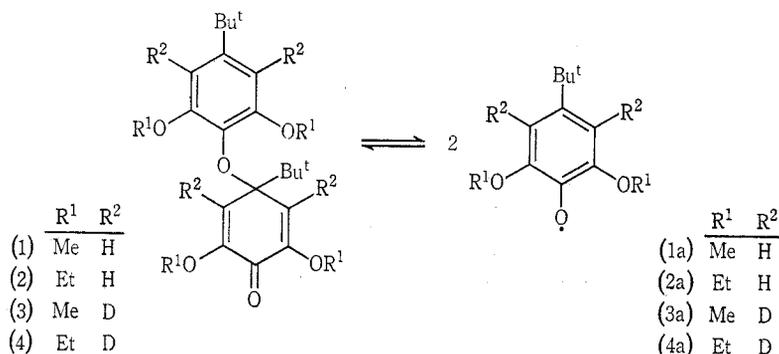
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### Abstract

E.s.r. spectra of aryloxy radicals derived from 4-*t*-butyl-2,6-dimethoxyphenol and 4-*t*-butyl-2,6-diethoxyphenol and also from the corresponding 3,5-dideuterophenols have been analysed. In both cases  $a_H \text{ meta} = a_H \alpha\text{-alkoxy}$ .

The oxidation of 4-*t*-butyl-2,6-dimethoxyphenol has been shown by one of us<sup>1</sup> to give the aryloxycyclohexadienone (1), which in benzene at room temperature dissociates sufficiently to give an intense e.s.r. spectrum of the aryloxy radical (1a).<sup>2</sup> The overlap of lines in this spectrum was such that hyperfine splitting constants could not be assigned with certainty. We have now prepared the analogous diethoxy dimer (2), and two dimers (3) and (4) deuterated in the *meta* positions. The radicals derived from these, exhibiting simpler spectra, allow an unequivocal assignment of splitting constants in this series.



Deuteration of 4-*t*-butyl-2,6-dimethoxyphenol and 4-*t*-butyl-2,6-diethoxyphenol was achieved by heating with a solution of deuterium chloride in dioxan. Under these conditions no loss of isobutene occurred, and the extent of exchange was greater than 95%.

The spectrum of the ethoxyaryloxy radical (2a) showed a clearly defined septet derived from four equivalent methylene protons and two *meta* protons with the same

<sup>1</sup> Adderley, C. J. R., and Hewgill, F. R., *J. Chem. Soc. C*, 1968, 1439.

<sup>2</sup> Adderley, C. J. R., and Hewgill, F. R., *J. Chem. Soc. C*, 1968, 1443.

splitting, further split by the *t*-butyl protons. Splitting by the ethoxy methyl protons was too small to be resolved. The deuterated methoxyaryloxy radical (3a) gave a septet spectrum, derived from the six equivalent methoxy protons, again further split by *t*-butyl protons, while the spectrum of the deuterated ethoxyaryloxy radical (4a) was fundamentally a quintet derived from the ethoxy methylene protons, further split by the *t*-butyl group. The simplification thus obtained in the spectra allowed splitting constants to be assigned, and these were further refined to those shown in Table 1 by matching with computer simulated spectra. Fig. 1 shows an example.

Table 1. Hyperfine splitting constants (G) of aryloxy radicals in benzene

| Radical | $a_H$ meta        | $a_H$ alkoxy      | $a_H$ t-butyl     |
|---------|-------------------|-------------------|-------------------|
| (1a)    | 1·19 <sub>2</sub> | 1·19 <sub>2</sub> | 0·29 <sub>8</sub> |
| (2a)    | 1·45 <sub>0</sub> | 1·45 <sub>0</sub> | 0·29 <sub>0</sub> |
| (3a)    |                   | 1·17 <sub>5</sub> | 0·27 <sub>5</sub> |
| (4a)    |                   | 1·42 <sub>0</sub> | 0·28 <sub>2</sub> |

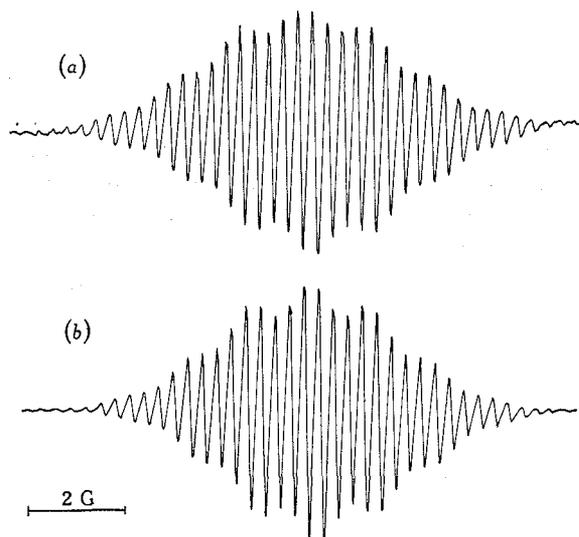


Fig. 1. E.s.r. spectrum of 4-*t*-butyl-2,6-dimethoxyphenoxy radical: (a) experimental; (b) simulated.

In both cases deuteration slightly decreased  $a_H$  alkoxy and  $a_H$  *t*-butyl. The equivalence of  $a_H$  meta and  $a_H$  alkoxy within experimental error is interesting and has been previously observed in the spectra of various syringyloxy radicals.<sup>3</sup> The additional lines in the wings of the previously recorded spectrum of radical (1a)<sup>2</sup> are presumed to be due to <sup>13</sup>C splitting.

### Experimental

N.m.r. spectra were recorded with a Varian A-60 spectrometer at 60 Hz using carbon tetrachloride solutions. E.s.r. spectra were recorded with a Varian V4500-10A spectrometer. Benzene solutions of the dimers were degassed by repeated freeze-pump-thaw cycles before insertion into the cavity. Dioxan was distilled from lithium aluminum hydride and left standing for 2 days over molecular sieves.

<sup>3</sup> Caldwell, E. S., and Steelink, C., *Biochim. Biophys. Acta*, 1969, **184**, 420.

*4-t-Butyl-2,6-diethoxyphenol*

t-Butyl alcohol (6g) was added dropwise over 30 min to a stirred solution of 2,6-diethoxyphenol (3.9 g) in refluxing light petroleum (40 ml) containing phosphoric acid (20 g, 98%). After 3 h the mixture was poured into water, the light petroleum layer was separated, washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and distilled giving a fraction, b.p. 99–104°/0.1 mmHg. This solidified on cooling, and crystallization from aqueous ethanol gave *4-t-butyl-2,6-diethoxyphenol* as needles, m.p. 36–37° (Found: C, 70.4; H, 9.2.  $\text{C}_{14}\text{H}_{17}\text{O}_3$  requires C, 70.6; H, 9.3%). N.m.r.  $\delta$  6.46 (2ArH), 4.97 (OH), 4.07 (q), 1.40 (t) ( $2 \times \text{OEt}$ ) and 1.25 (Bu<sup>t</sup>).

*4-t-Butyl-2,6-diethoxy-4-(4'-t-butyl-2',6'-diethoxyphenoxy)cyclohexa-2,5-dienone*

A solution of 4-t-butyl-2,6-diethoxyphenol (1 g) in ether (25 ml) was shaken with an aqueous solution of potassium ferricyanide (4 g) and sodium hydroxide (0.8 g) for 5 min. The green ether layer was separated, washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent under vacuum and crystallization of the residue from n-pentane gave the *dienone* as pale yellow needles (0.8 g), m.p. 111.5–112.5° (Found: C, 70.5; H, 9.0.  $\text{C}_{28}\text{H}_{42}\text{O}_6$  requires C, 70.8; H, 8.9%).

*Deuterated Compounds*

Deuterium chloride was generated by the addition of a slight excess of deuterium oxide to redistilled acetyl chloride (5 ml) in dry dioxan (4 ml). The phenol (1 g) in dry dioxan (5 ml) was added to this solution and the whole was heated under reflux for 9 h with exclusion of moisture. The cooled solution was poured into ice water and extracted with ether. Distillation of the dried ( $\text{Na}_2\text{SO}_4$ ) extract at 0.1 mmHg gave the deuterated phenol. The extent of exchange was determined to be >95% by comparison of the aromatic and t-butyl proton integrations in the n.m.r. spectrum. Repetition of the deuteration failed to improve the deuterium content significantly. Other resonances in the n.m.r. spectrum were identical with those of the undeuterated phenols.

The deuterated phenols were oxidized as described for 4-t-butyl-2,6-diethoxyphenol. The resulting dimers appeared identical to the undeuterated compounds, except for the absence of *meta* proton resonances in the n.m.r. spectra.

Computer simulation of spectra was carried out by one of us (F.R.H.) while on leave at the University of York, England, using a program developed by Dr M. F. Chiu.

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